In-situ characterization tools for evaluating radiation tolerance and elemental migration in perovskites

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2024 IEEE 52nd Photovoltaic Specialist Conference (PVSC) | 978-1-6654-6426-0/24/$31.00 ©2024 IEEE | DOI: 10.1109/PVSC57443.2024.10749549

Abstract — **This paper discusses the in-situ characterization tools designed to assess radiation tolerance and elemental migration in perovskite materials. With the increasing use of perovskites in various technological applications, understanding their response to radiation exposure is paramount. Ion Beam Induced Charge (IBIC) emerges as a powerful tool for investigating the radiation tolerance of perovskites at the microscale. By employing focused ion beams, IBIC allows for the spatial mapping of charge carriers, offering insights into the material's electronic response to radiation-induced defects. This technique enables researchers to pinpoint areas of enhanced or suppressed charge collection, providing valuable information on the perovskite's intrinsic properties under irradiation. Rutherford Backscattering Spectrometry (RBS) complements the study by offering a quantitative analysis of elemental migration in perovskite materials. Through the precise measurement of backscattered ions, RBS provides a detailed understanding of the elemental composition and distribution within the perovskite lattice after radiation exposure. The integration of IBIC and RBS techniques in in-situ experiments enhances the comprehensive characterization of radiation effects on perovskites.**

I. Introduction

Mixed halide perovskites (MHP) have recently gained a lot of attention in the field of photovoltaics due to their excellent optoelectronic properties, low-cost fabrication, and band gap tuning [1]. In addition to its terrestrial applications, scientists are also investigating its potential applications in space photovoltaics. Recent irradiation studies have shown that perovskite solar cells are more resilient to radiation than other conventional solar cell devices [2,3]. To further advance the understanding of the nature of radiation damage and elemental migration, developing an in-situ setup is the next step. We can employ ion beam techniques like Ion Beam Induced Charge (IBIC) and Rutherford backscattering (RBS) to directly monitor the behavior of the device in conditions that are very similar to space (i. e. vacuum, radiation, illumination, temperature cycle etc.) [4]. The Ion Beam Laboratory (IBL) at the University of North Texas (UNT), Physics Department houses four particle accelerators, including a 3 MV tandem Pelletron (NEC 9SDH-2 Pelletron), a 3 MV single-ended Pelletron (NEC 9SH Pelletron), a 200 kV Cockcroft-Walton, and a 2.5 MV Van de Graaff. Each accelerator, with dedicated beamlines, serves unique purposes. The 9SH Pelletron and 9SDH-2 tandem are located in the main lab (Fig. 1). The tandem accelerator has three negative-ion sources installed, two are Cs-sputtered for solid targets and one for RF type for noble gases. The negative ions are generated using the NEC Source of Negative Ions by Cesium Sputtering (SNICS-II). Using the NEC SNICS-II ion source, negative ions of Hydrogen, Carbon, Oxygen, Silicon, Germanium, Copper, Silver, Nickel, Gold, etc., are generated and can be accelerated to energies ranging from 10 to 85 keV.

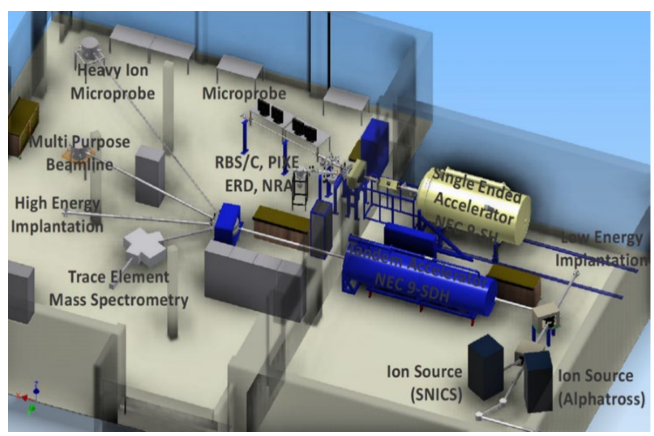

Fig. 1. Schematics for the Ion beam laboratory at the IBL, UNT

The single-ended accelerator can produce positive ions of hydrogen, helium, or nitrogen using an RF source. Currently, it has three dedicated beamlines associated with it. The first beamline is a high-energy microprobe beamline. It focuses the particle beam to sub-micron to perform techniques such as micro-Rutherford Backscattering spectroscopy (μ-RBS), micro-particle induced X-ray emission (μ-PIXE), scanning transmission ion spectroscopy (STIM), and Ion Beam Induced

Charge (IBIC) to obtain respective maps of certain regions of the samples, for analyzing trace elements, amongst other applications [5]. The second beamline is a high-energy implant station, while the third beamline is used for broad-beam analysis.

IBIC is a powerful scanning ion microprobe-based technique that can be used to provide information about the fundamental electronic properties of semiconductor materials and devices including radiation detectors, solar cells, and charge-coupled arrays, and can pinpoint damage or failure sites within semiconductor devices. The MeV ion beam while moving within the target loses energy to the atoms resulting in the shifting of electrons from the valence band to the conduction band which leaves a hole in the valence band behind generating an e-h pair. The generated mobile ions are then separated in the semiconductor if there is an electric field present as shown in Fig. 2. These carriers are then processed by a charge-sensitive pre-amplifier which is further processed by the multichannel analyzer [6,7].

IBIC requires optimization of the beamline as it only requires the beam current in the range of ~1 fA (10^4 particles/s) to minimize the damage to the device, but still, one single scan is equivalent to ~10^{10} ions/cm^2, which is enough to generate a charge map of the device using an event-by-event mode data acquisition system for better analysis of the data [7].

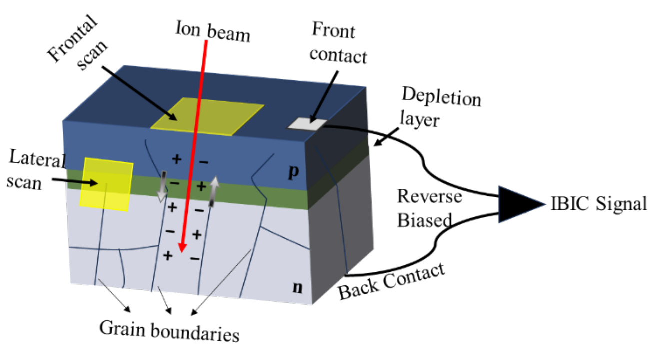

Fig. 2. Schematics of the basic processes in IBIC microscopy.

In addition to IBIC, RBS can be employed to study the elemental migration within the device. In MHP, elemental migration is one of the leading causes of degradation and hysteresis which can be accelerated by external factors such as temperature, humidity, and/or moisture. While there are other techniques available like electrochemical impedance spectroscopy (EIS) [8], time of flight secondary ion mass spectroscopy (ToF-SIMS) [9], and thermal admittance spectroscopy (TAS) [10], etc., these techniques require extensive sample preparation whereas RBS doesn't require any such complicated sample preparation. Moreover, RBS is a non-destructive technique. RBS can be used to identify the elemental compositions present within the sample along with their depth profile. Initial RBS measurements were performed on metal halide perovskite material to gain insights into the depth profile of Pb and I. However, this measurement was not made on the full stack of the solar cell structure [11]. Here, we will discuss initial IBIC measurements performed on silicon PIN diodes and initial RBS measurements on the full stack of MHP solar cells with triple cation perovskite ($(Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})_3)$) as the photo absorber layer to better understand the role of elemental migration in these complex structures.

II. EXPERIMENTAL

IBIC was performed by exposing the device to 2 MeV H^+ ions in the microprobe chamber. Before moving to the PIN diode, the beam current was measured using Ion-Implanted-Silicon Charged-Particle Detectors [12]. After confirming the beam current, the IBIC test was performed on Hamamatsu S1223 PIN diodes [13]. The diodes were negatively biased at -20 V so that only minority carriers were transported though the depletion region [14]. The charge created is collected by a CoolFET Amptek A250CF low noise charge sensitive preamplifier (CSP) [15]. A schematic of this system is shown in Fig. 3.

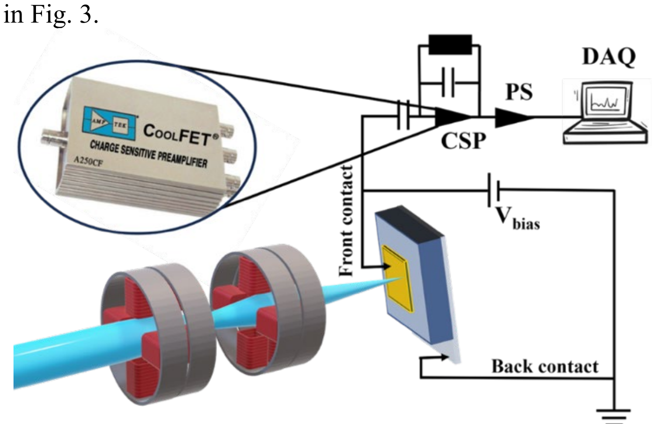

Fig. 3. The schematics for the IBIC setup where CSP corresponds to charge sensitive preamplifier, DAQ corresponds to the data acquisition program, and PS to Pulse shaper. Inset displays the picture of Amptek CoolFET A250 low noise charge sensitive preamplifier.

A 2 MeV He^+ beam was used to perform the RBS experiment in the microprobe chamber. Backscattered particles are detected by a passivated implanted planar silicon (PIPS) particle detector from Mirion Technologies (Canberra), having a solid angle of 34 milli-steradian. A total fluence of 3.95×10^{14} ions/cm^2 was collected. The RBS fitting was done by using the SIMNRA simulation software package. For further analysis of individual contributions from the perovskite layer another software package MultiSIMNRA was used.

III. RESULTS

The initial irradiations were performed on an area of 16×16μm^2 on PIN diodes and fluence was controlled by increasing the number of scans and the corresponding charge collection efficiency (CCE) plots were displayed in Fig. 4a. To prevent potential edge-related influences, the spectra were acquired from the central regions of the irradiated areas. With increasing fluence, the CCE is seen to be decreasing, which is expected for these devices.

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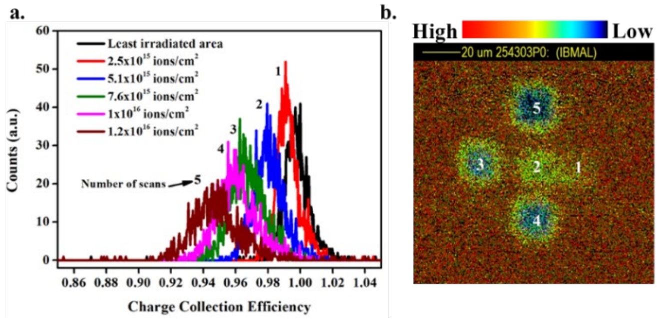

Fig. 4. a) Trend of CCE plot for PIN diodes with increasing fluence. b) CCE maps containing irradiated areas.

To obtain the plot of all damage profiles in a single map, a large area scan of 125×125μm^2 was performed, shown in Fig. 4b. RBS was also performed on the MHP solar cell structure shown in Fig. 5a.

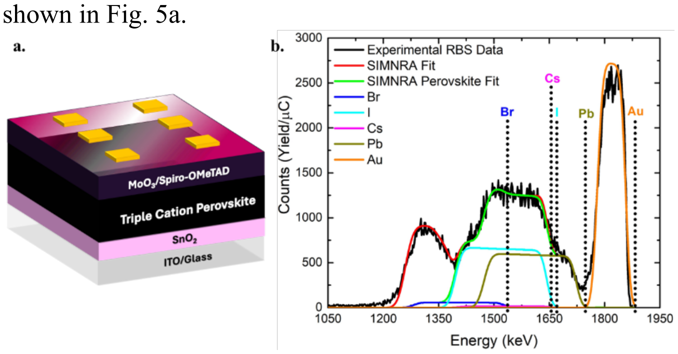

Fig. 5. a) Schematic depiction of the triple-cation N-I-P PSC used in this study, and (b) Data of the RBS scan acquired on the active area, showing contributions from the top contact (Au) and perovskite layer with its major elemental species i.e. Pb, Cs, I, and Br.

The RBS spectra on the MHP solar cell are shown in Fig. 5b. The elemental contribution of the MHP was further divided into individual element species including Br, Cs, I, Pb, and Au within the energy ranges of 1264-1548 keV, 1362-1676 keV, 1398-1660 keV, 1440-1754 keV, and 1744-1870 keV, respectively.

IV. CONCLUSION

A brief overview of the in-situ ion-beam characterization tools designed to assess radiation tolerance and elemental migration in perovskite materials is provided. In the future, we plan to extend this technique to other semiconductor detectors, and photovoltaic devices to better understand the nature of defects, charge kinetics, and to visualize the radiation effects on device structures. This study will be further advanced to study the impact of stressors like moisture and using long exposures to study elemental migration within these devices.

V. ACKNOWLEDGMENTS

The ion beam activities at the University of North Texas has been supported in parts by grants from federal agencies such as NIH-R01DK109382, NIH-R21HD083389, NSF-DMR-0960222, HBCU-EiR-2101181, and NSF-ECCS-2210722. We would also acknowledge the contribution of past members of IBL comprising of undergraduate and graduate students, postdoctoral fellows, faculty and visiting fellows. The perovskite solar cell devices were developed under support from the Operational Energy Capability Improvement Fund of the Department of Defense at NREL.

REFERENCES

[1] Kojima, A., Teshima, K., Shirai, Y., and Miyasaka, T. (2009) Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *Journal of the American Chemical Society*. 131 (17), 6050–6051.

[2] Kirmani, A.R., Ostrowski, D.P., VanSant, K.T., Byers, T.A., Bramante, R.C., Heinselman, K.N., et al. (2023) Metal oxide barrier layers for terrestrial and space perovskite photovoltaics. *Nature Energy 2023 8:2*. 8 (2), 191–202.

[3] Durant, B.K., Afshari, H., Singh, S., Rout, B., Eperon, G.E., and Sellers, I.R. (2021) Tolerance of Perovskite Solar Cells to Targeted Proton Irradiation and Electronic Ionization Induced Healing. *ACS Energy Letters*. 6 (7), 2362–2368.

[4] Costa, C., Manceau, M., Duzellier, S., Nuns, T., and Cariou, R. (2023) Perovskite solar cells under protons irradiation: From in-situ IV-monitoring to root cause degradation elucidation. *Solar Energy Materials and Solar Cells*. 257 112388.

[5] Rout, B., Dhoubhadel, M.S., Poudel, P.R., Kummari, V.C., Pandey, B., Deoli, N.T., et al. (2013) An overview of the facilities, activities, and developments at the University of North Texas Ion Beam Modification and Analysis Laboratory (IBMAL). *AIP Conference Proceedings*. 1544 (1), 11–18.

[6] Donolato, C. (1979) Contrast and resolution of SEM charge-collection images of dislocations. *Applied Physics Letters*. 34 (1), 80–81.

[7] Breese, M.B.H., Jamieson, D.N., and King, P.J.C. (1996) Materials Analysis Using a Nuclear Microprobe. John Wiley and Sons, New York.

[8] Bag, M., Renna, L.A., Adhikari, R.Y., Karak, S., Liu, F., Lahti, P.M., et al. (2015) Kinetics of Ion Transport in Perovskite Active Layers and Its Implications for Active Layer Stability. *Journal of the American Chemical Society*. 137 (40), 13130–13137.

[9] Matteocci, F., Busby, Y., Pireaux, J.J., Divitini, G., Cacovich, S., Ducati, C., et al. (2015) Interface and Composition Analysis on Perovskite Solar Cells. *ACS Applied Materials and Interfaces*. 7 (47), 26176–26183.

[10] Awni, R.A., Song, Z., Chen, C., Li, C., Wang, C., Razooqi, M.A., et al. (2020) Influence of Charge Transport Layers on Capacitance Measured in Halide Perovskite Solar Cells. *Joule*. 4 (3), 644–657.

[11] Lang, F., Juma, A., Somsongkul, V., Dittrich, T., and Arunchaiya, M. (2015) Rutherford Backscattering Spectroscopy of Mass Transport by Transformation of PbI2 into CH3NH3PbI3 within np-TiO2. *Hybrid Materials*. 1 (1),.

[12] (n.d.) ULTRA and ULTRA-AS Ion Implanted Silicon Charged Particle Radiation Detectors | Alpha Spectroscopy | AMETEK ORTEC.

[13] (n.d.) Si PIN photodiode S1223-01 | Hamamatsu Photonics.

[14] Vizkelethy, G., King, M.P., Aktas, O., Kizilyalli, I.C., and Kaplar, R.J. (2017) Nuclear microprobe investigation of the effects of ionization and displacement damage in vertical, high voltage GaN diodes. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*. 404 264–268.

[15] (n.d.) A250 Charge Sensitive Preamplifier – Amptek – X-Ray Detectors and Electronics.