High Voltage Stability and Degradation Pathways in Perovskite Photon-Counting Detectors

Jayana Jayarathne[1],

C. Chandler [2], S. Derenko [3], J. Ghosh [4], D. Wolfe [6,7], M. Baker [2], M. Sessolo [3], C. Crean [5], P. Sellin [1]

[1] School of Mathematics and Physics, University of Surrey, UK

[2] School of Mechanical Engineering Sciences, University of Surrey, UK

[3] Instituto de Ciencia Molecular, Universidad de Valencia, Spain

[4] Inorganic Chemistry Laboratory, University of Oxford, UK

[5] School of Chemistry and Chemical Engineering, University of Surrey, UK

[6] Applied Research Laboratory, The Pennsylvania State University, USA

[7] Materials Science and Engineering, The Pennsylvania State University, USA

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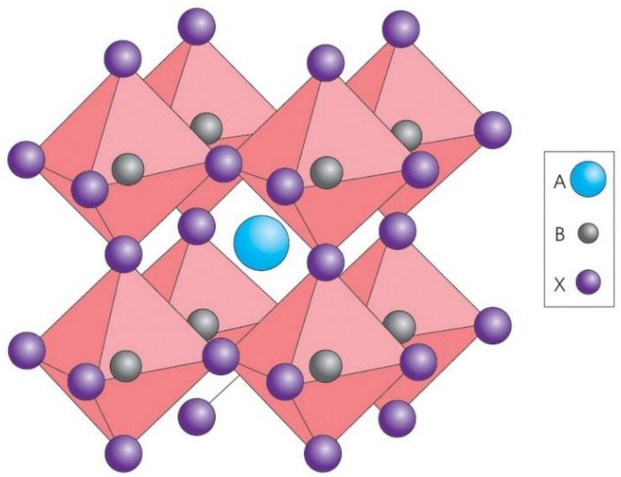
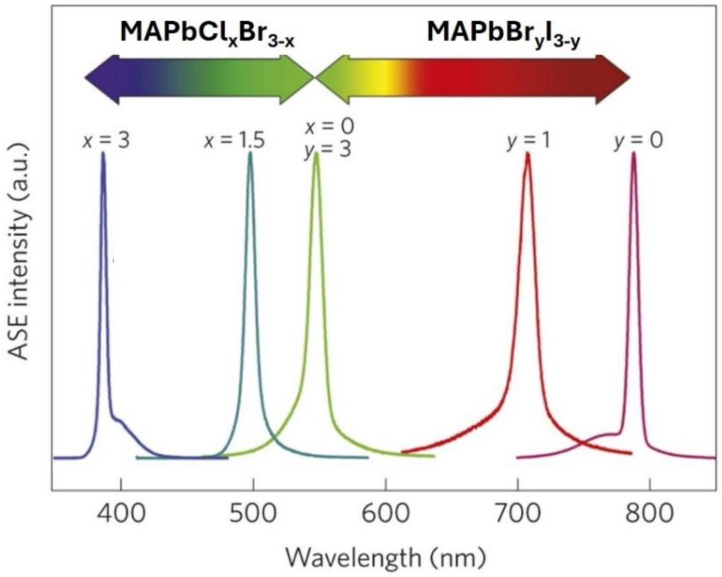
Outline

- Metal Halide Perovskites
- Synthesis of $FAPbBr_3$ Single Crystals
- Optimising Charge Transport Properties
- Spectroscopic Radiation Detection Performance
- Device Operational Stability and Prebiasing
- Degradation Pathways of Perovskite Single Crystal Detectors
- Summary and Conclusion

Metal Halide Perovskites

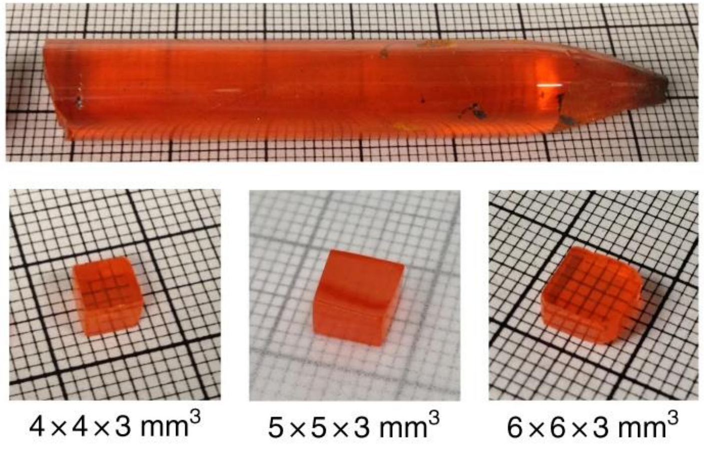


Green et al., Nat. Photonics, vol. 08, 2014

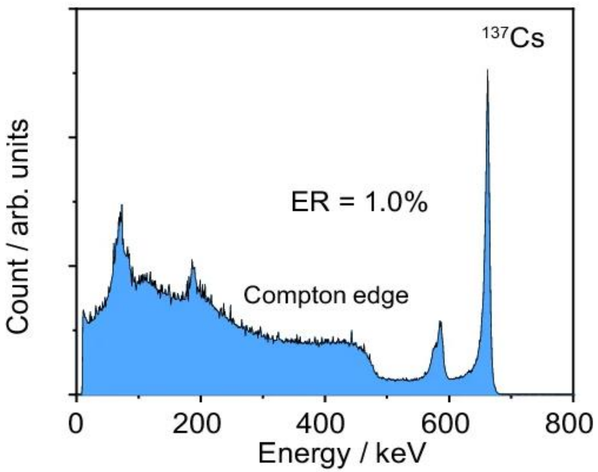


G. Xing et al., Nat. Materials, vol. 13, 2014

Melt Grown $CsPbBr_3$



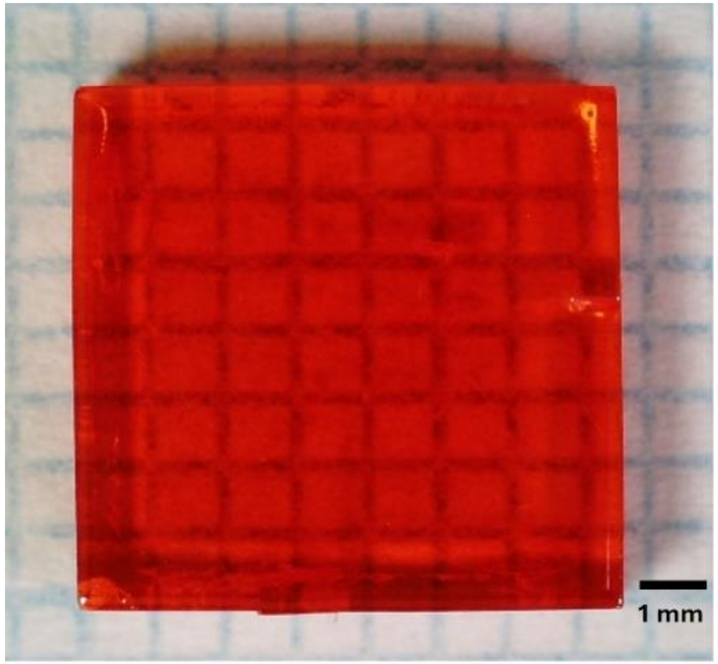
H. Yihui et al., Nat. Commun., vol. 09, 2018



S. Nannan et al., Nat. Commun., vol. 16, 2025

- Metal halide perovskites are semiconductors with an ABX_3 structure: A is an organic or inorganic cation, B a metal cation, and X a halide.
- Have a tunable bandgap.
- Many applications including photodetectors, solar cells and LEDs.
- Promising for radiation detection applications.

$FAPbBr_3$ Single Crystals



Bridgman grown $CsPbBr_3$ Single Crystals (SCs):

- Shown better radiation detection performance.
- However, requires high temperature and is energy intensive.

Solution grown SCs:

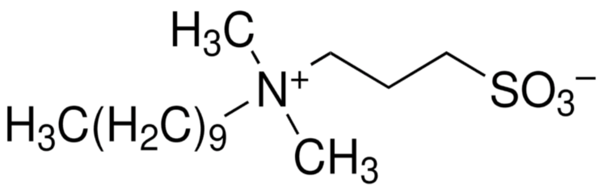
- Grown using the Inverse Temperature Crystallisation (ITC) Method
- Low cost, low temperature growth.

$FAPbBr_3$ (FPB) compared to other perovskites:

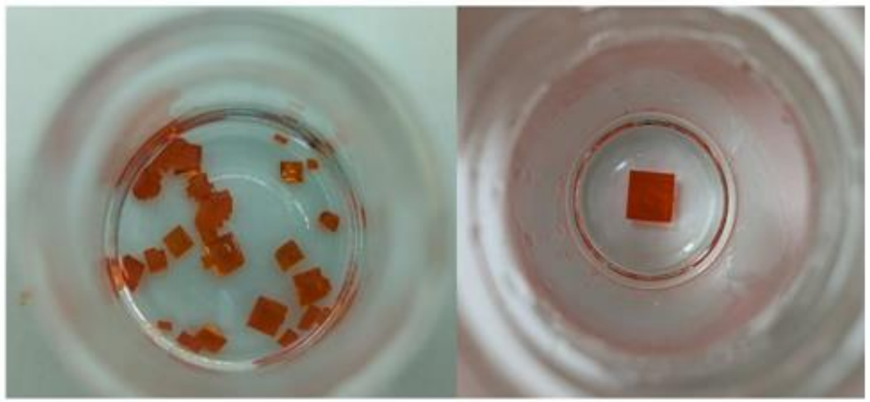
- Absence of room temperature phase transitions.
- Higher temperature stability over $MAPbBr_3$.
- Tolerance factor closer to 1.

Solution-Growth Process Optimisations

DPSI Molecule



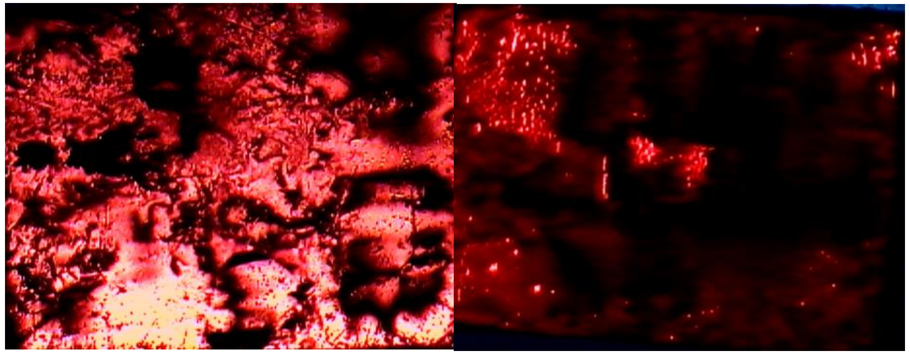
- Addition of DPSI suppresses spontaneous nucleation and regulates growth.

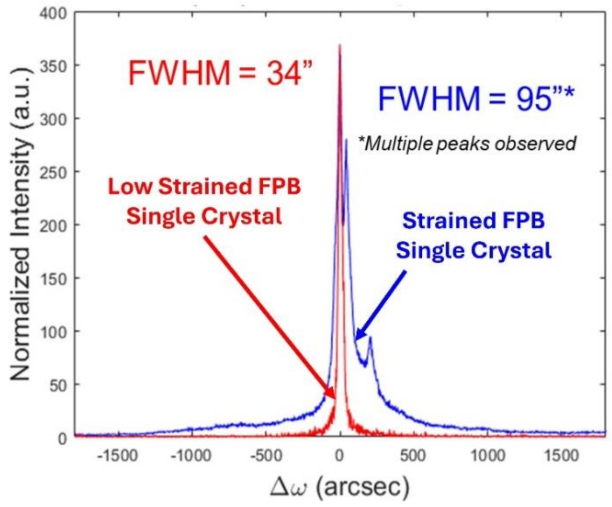


Without DPSI **With DPSI**

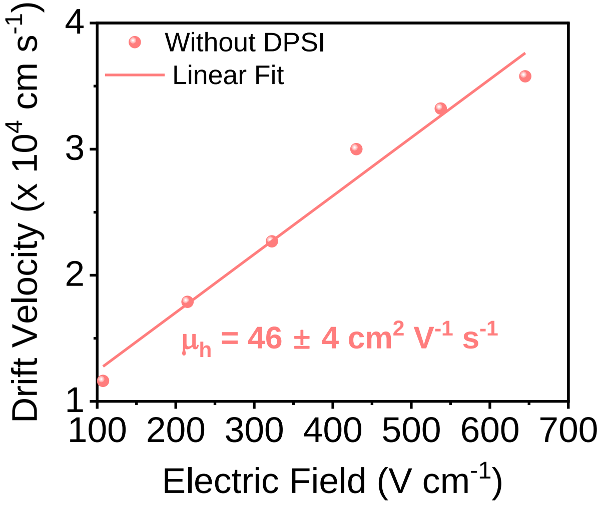
- Residual strain observed in FPB SCs grown with DPSI additive.
- Lower strained SCs grown with DPSI and an improved ITC growth method.
- High-resolution XRD rocking curves confirm improved crystalline quality in low-strained SCs.

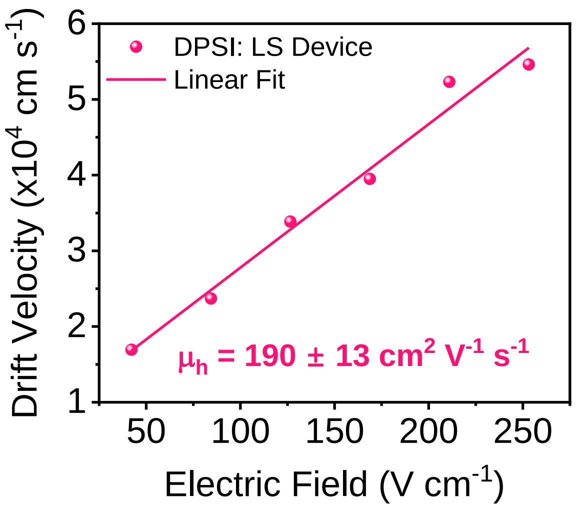
Standard ITC Method **Improved ITC Method**



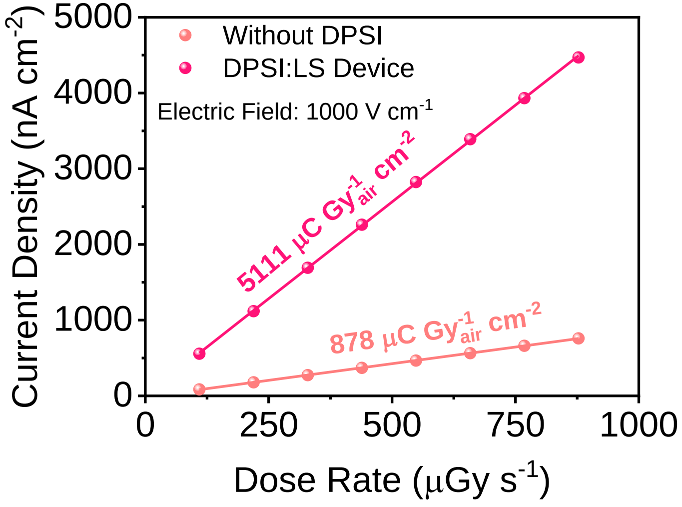


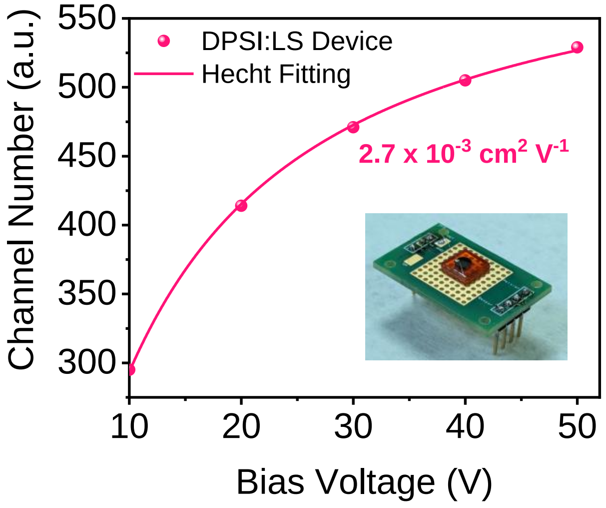
Improvement in Charge Transport Properties





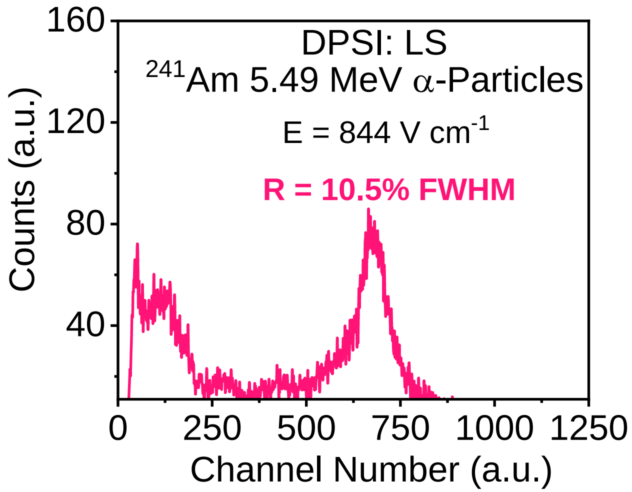
- Lower strained FPB SC device (DPSI:LS) show more than **4 x higher** hole mobilities compared to pristine SCs.

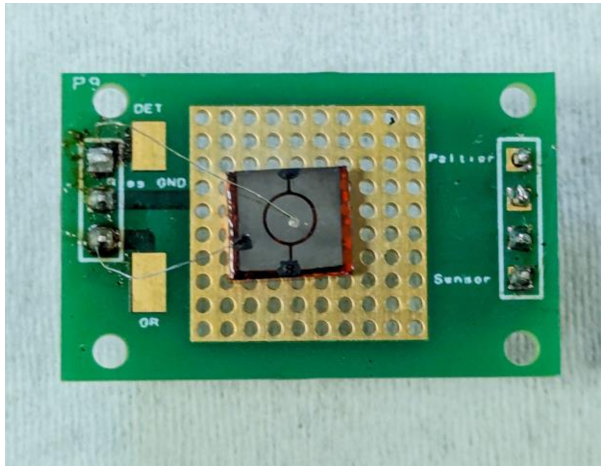




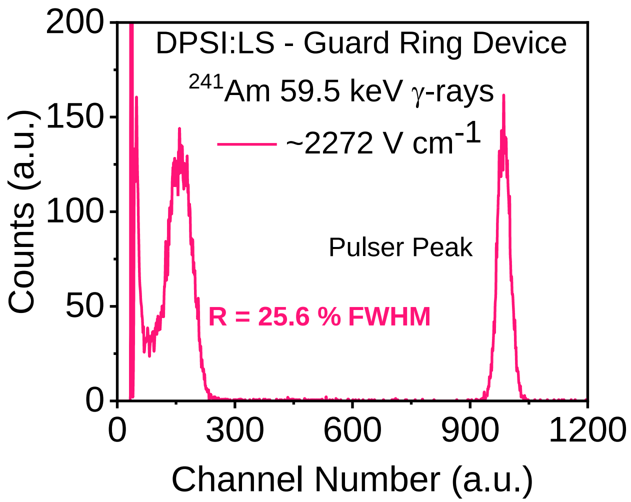
- These devices show **~ 6 x higher** X-ray sensitivity compared to SCs grown without DPSI. Excellent μτ product of 2.7×10^{-3} $cm^2 V^{-1}$ was also achieved.

Spectroscopic Radiation Detection Performance



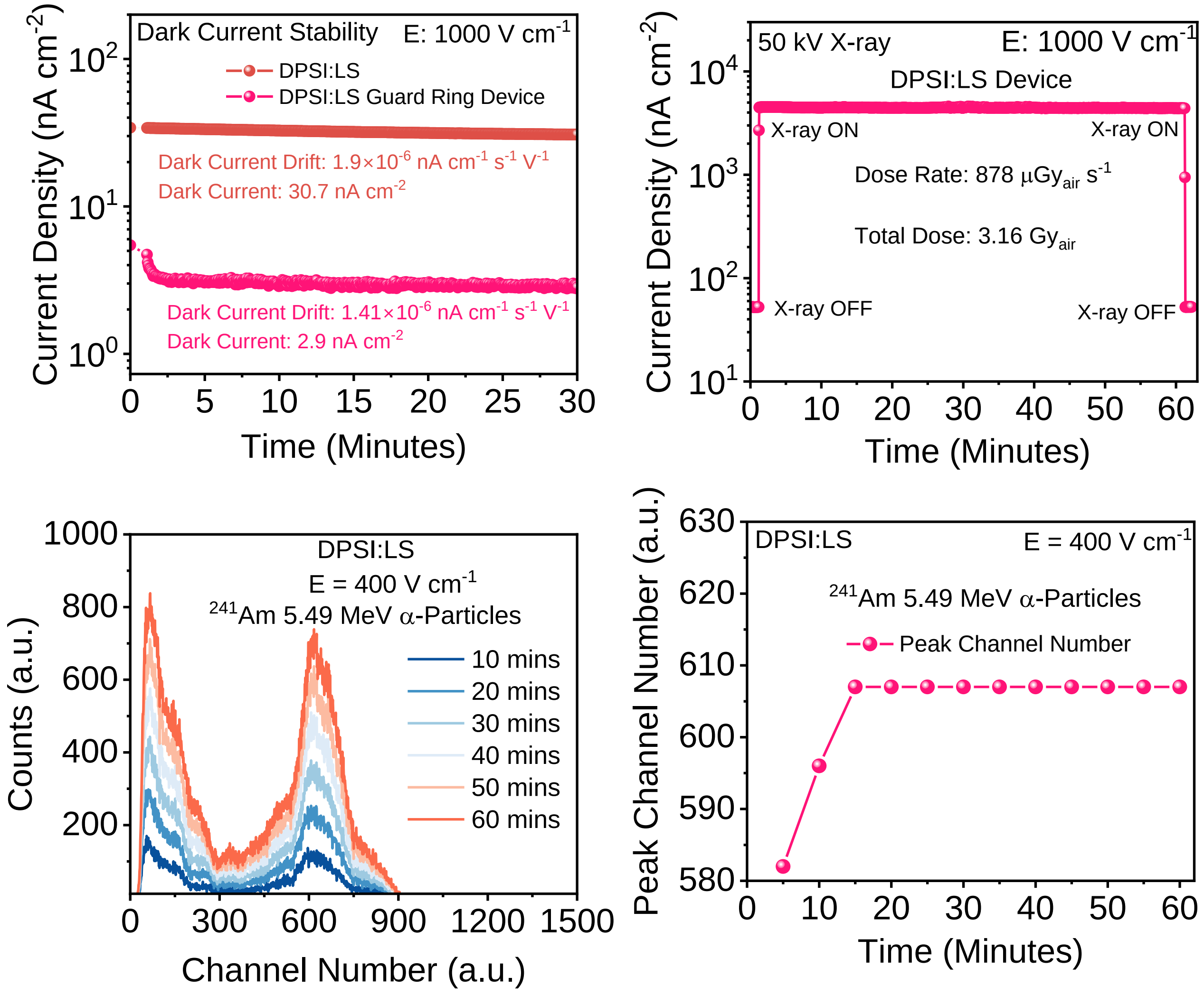


- DPSI:LS device managed to resolve ^{241}Am 5.49 MeV α-particles with a **10.5%** energy resolution.
- Guard-ring contact structure used to reduce leakage currents of devices.



- The FPB SC device also managed to resolve ^{241}Am 59.5 keV γ-rays with a 25.6% energy resolution.

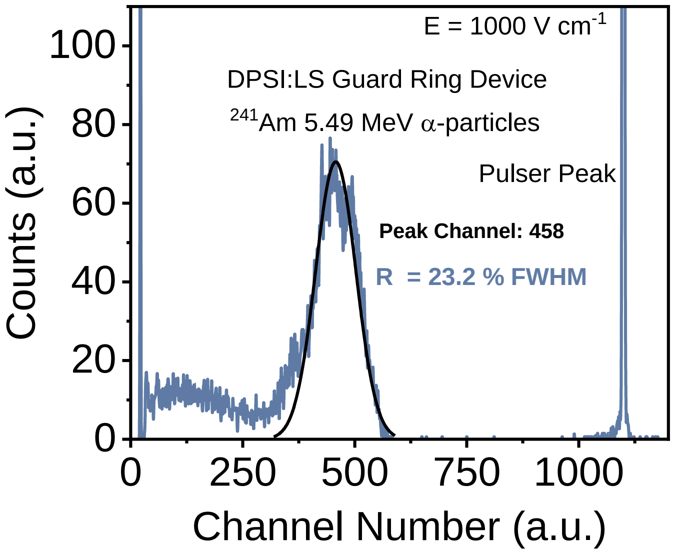
Temporal Operation of FPB SC Detectors



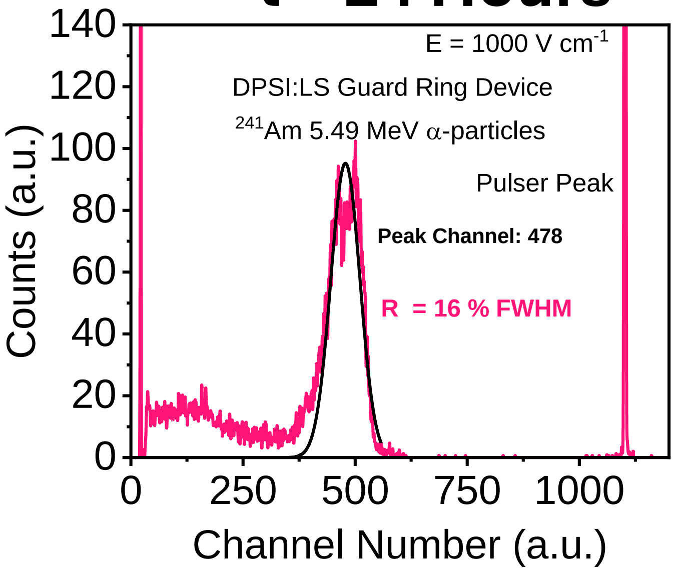
- **Ultra-low dark current**: 2.9 nA cm^{-2} at 1000 V cm^{-1} (~10× lower than non-guard-ring devices).
- **Stable X-ray photocurrent**: No significant drift under 50 kV X-ray irradiation (~900 µGy s^{-1}).
- **Stable spectroscopic response**: Peak channel position remained stable during 1 hour of continuous operation

Prebiasing Effects of PSC Detectors

t = 0

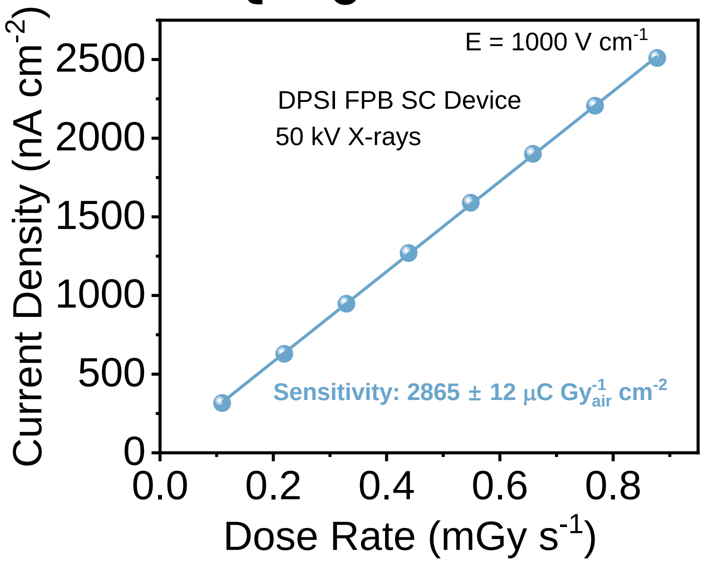


t = 24 Hours

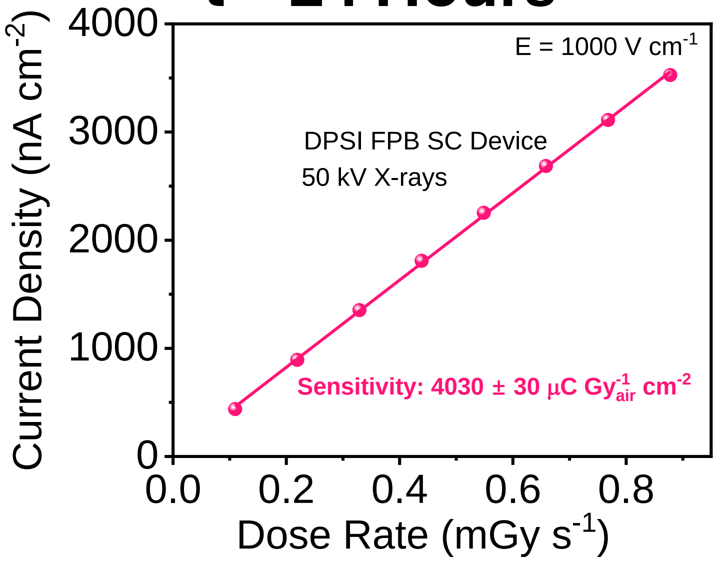


- 24-hour pre-biasing improves FPB SC detector energy resolution by **~31%** for 5.49 MeV ^{241}Am α-particles.

t = 0

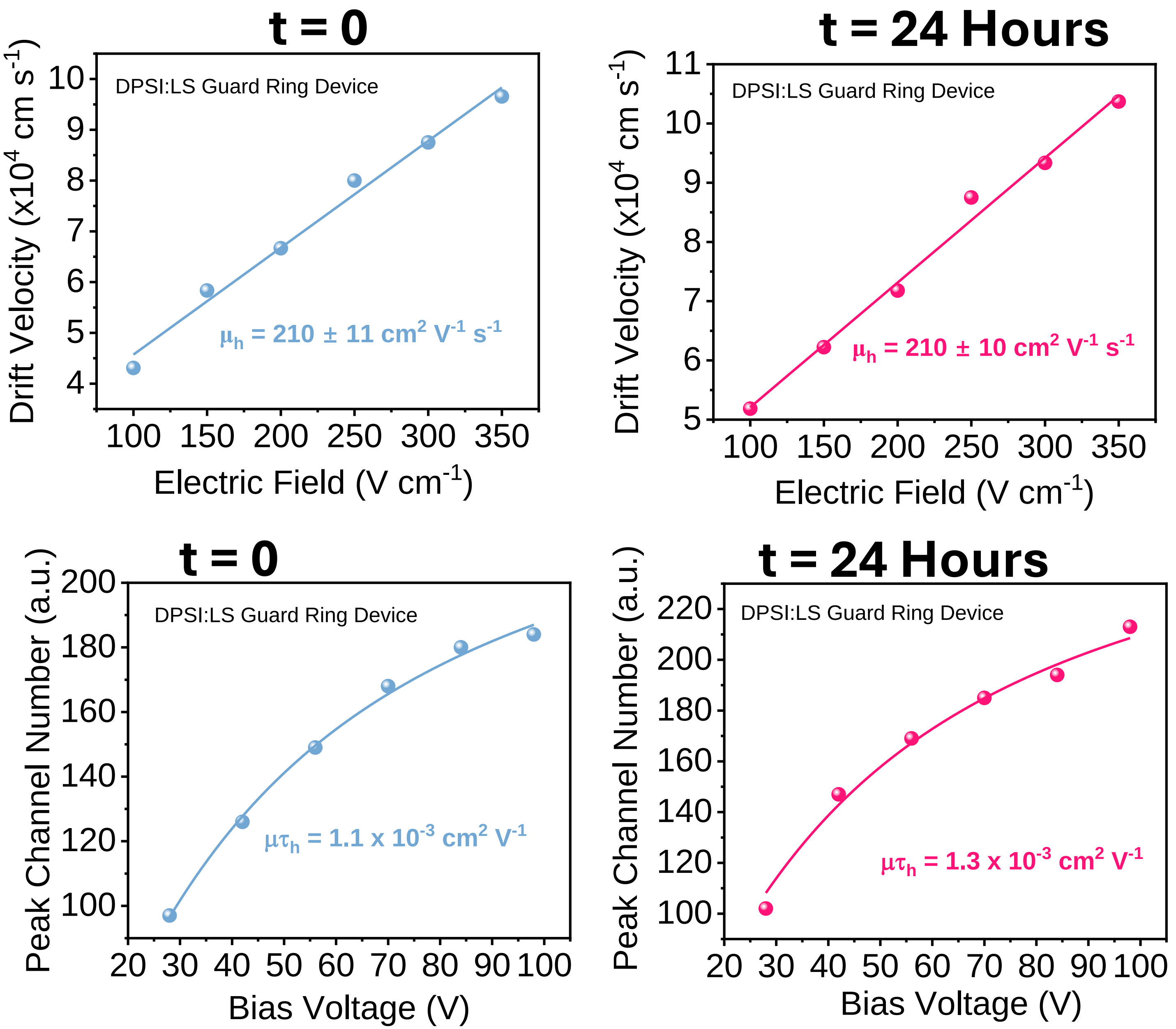


t = 24 Hours



- Prebiasing also improved energy-integration performance, yielding **~41%** higher X-ray sensitivity after 24-hour prebias.

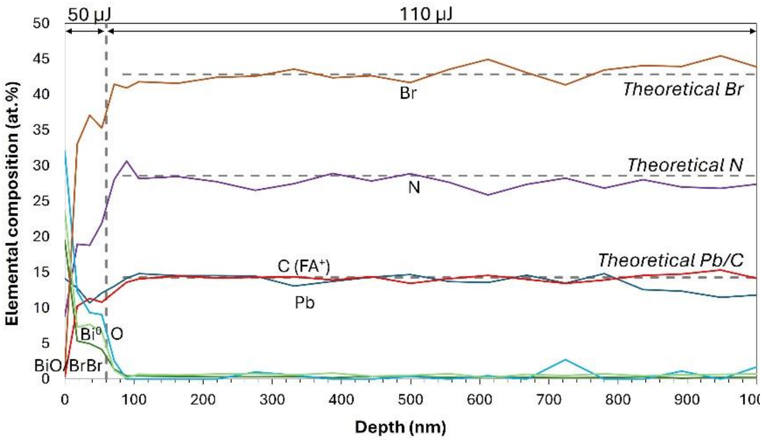
Prebiasing Effects: Bulk Charge Transport

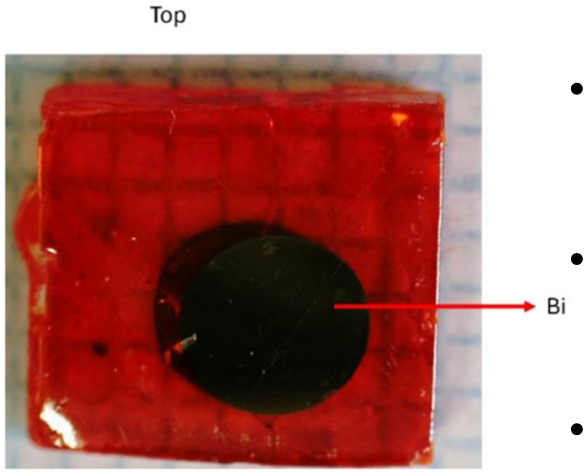


- **Pre/Post pre-bias transport comparison**: Charge transport in FPB SC detectors evaluated using 5.49 MeV ^{241}Am α-particles before and after pre-biasing.
- **Bulk transport stability**: Hole mobility (μ_h) and mobility–lifetime product ($\mu_h\tau_h$) show no significant change after pre-biasing.
- **Proposed mechanism**: 24 hour pre-bias performance improvements are hypothesised to originate from ion migration enhancing signal generation without altering bulk transport properties.

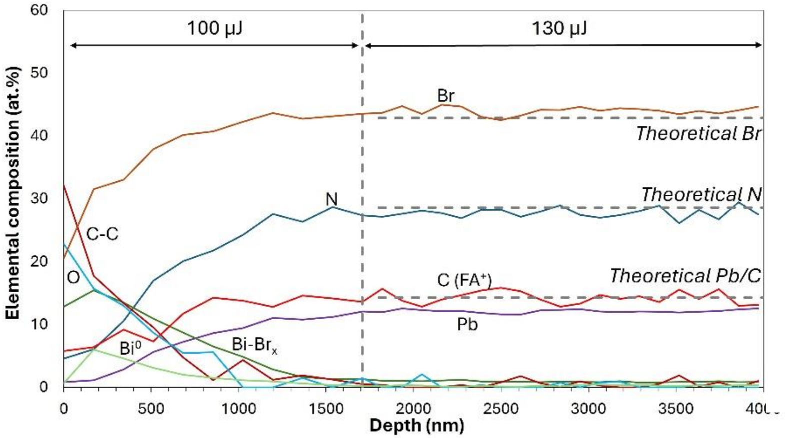
Halide Migration in Perovskite Single Crystals

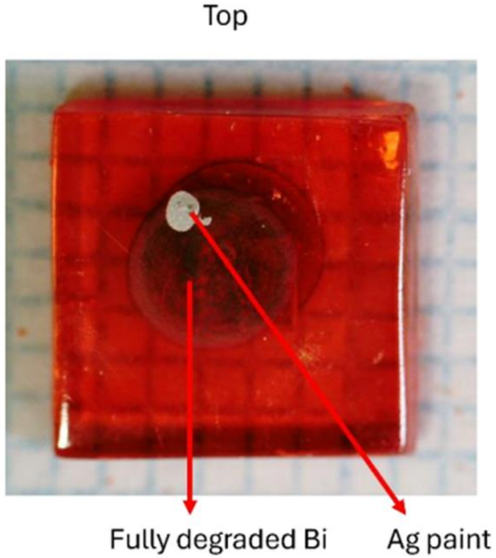
Fresh Device





Degraded Device: 1000 V cm^{-1} continuous bias for 4 days



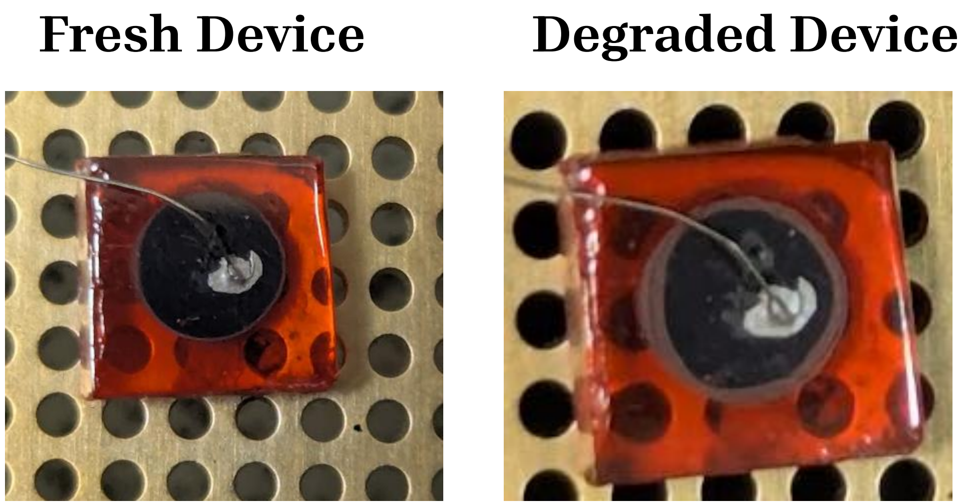


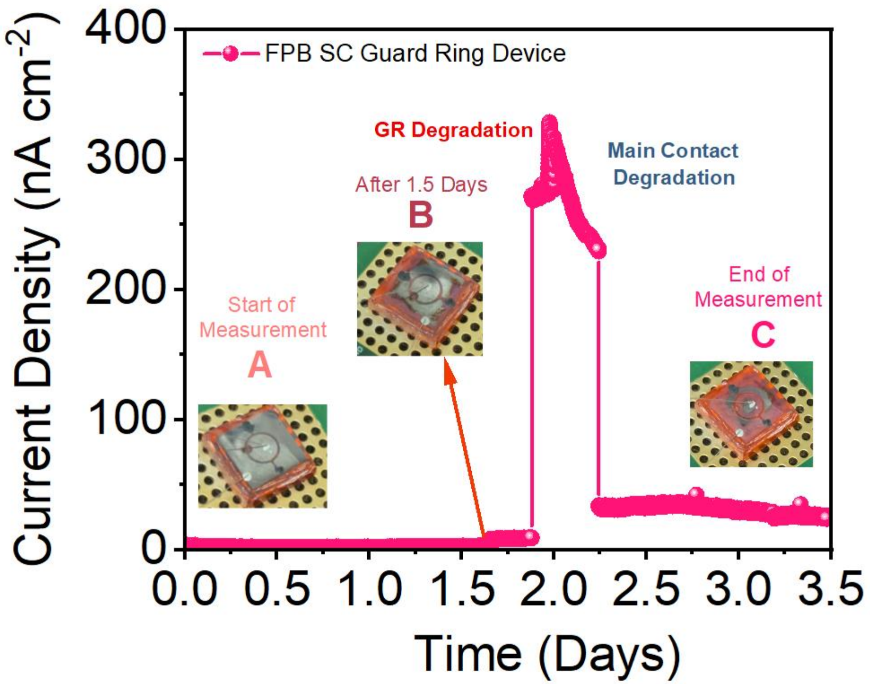
- Ion migration poses as a major challenge for the stability of perovskite devices.
- Halide (Br^-) migration is prominently seen in perovskites and accelerates with biasing.
- XPS depth profiling was conducted on a fresh FPB SC device and a device continuously biased for 4 days under an applied electric field of 1000 V cm^{-1}.
- XPS depth profiling reveals that Br^- ions react with the bismuth metal electrode, forming $BiBr_x$ species.

Proposed Chemical Reaction

$$3Pb^{2+} + 6Br^- + 2Bi = 2BiBr_3 + 3Pb$$

High Electric Fields at Metal Contact Edges

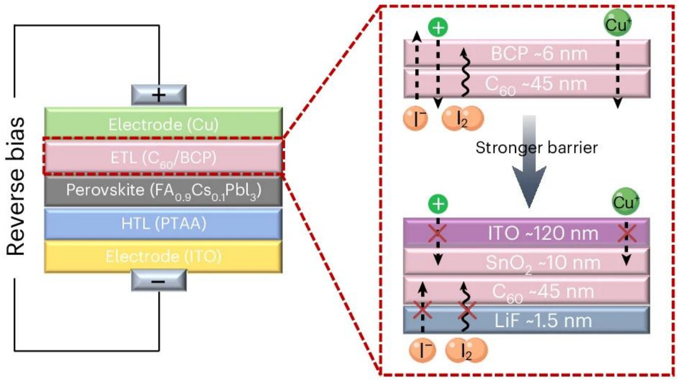




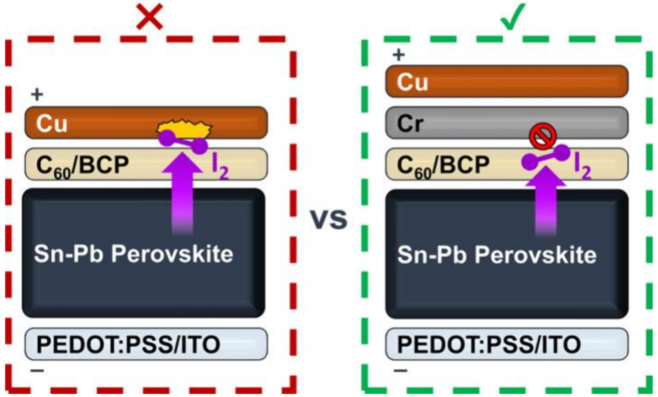
- Localised high electric fields form at the metal electrode edge.
- Mobile ions, including Br^- drift towards the high electric field regions at the edge of the contact, initiating contact degradation at the edge.
- Guard ring (GR) contacts collects the surface leakage current and high electric field regions form at the edge of the guard ring instead of the main electrode.
- Initial ion redistribution may improve performance (interface conditioning), followed by degradation once chemical reactions dominate

Barrier Layers to Mitigate Electrode Degradation

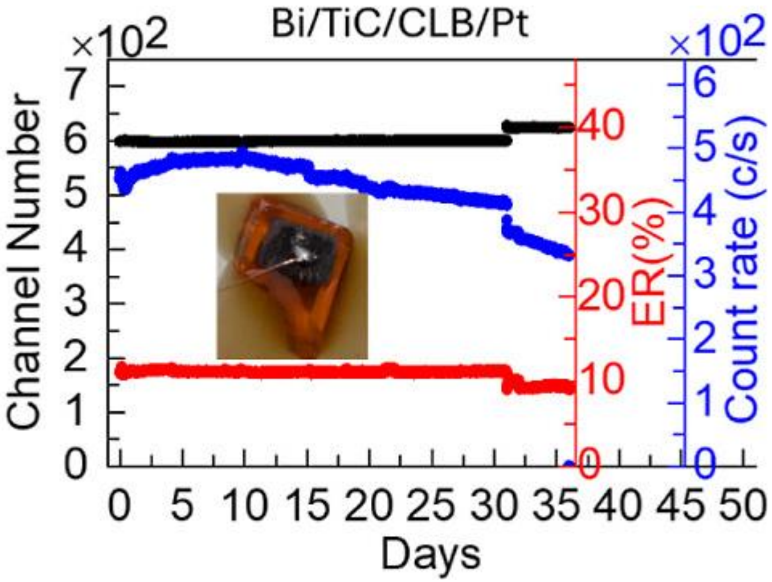
L. Nengxu et al., Nat. Energy., vol. 09, 2024



L. Lanzetta et al., ACS Energy Lett., vol. 10, 2025



K. Sujita et al., ACS Appl. Electron Mater., vol. 07, 2025



- Electrode degradation mechanisms have been observed in perovskite solar cells and radiation detectors operated under reverse-bias conditions.
- Ionic barrier layers have been shown to mitigate these degradation effects.
- These layers can be deposited using thermal evaporation, atomic layer deposition (ALD), and electron-beam (e-beam) deposition.
- Surface optimisation and barrier-layer deposition will be explored in future work, in collaboration with the University of Valencia and Penn State University.

Summary and Conclusions

- High-quality FPB SCs synthesised with DPSI exhibit improved bulk charge transport properties.
- Improved charge transport properties achieved for low strained FPB SCs with hole mobilities reaching 190 $cm^2 V^{-1} s^{-1}$. A fast response of 2.1 μs was achieved.
- FPB SC devices can resolve ^{241}Am 5.49 MeV α-particles with an energy resolution of 10.5 % and 59.5 keV γ-rays with a resolution of 25.6 %.
- Prebiasing effects show improvements in the spectroscopic energy resolution and X-ray sensitivity. No significant improvements in charge transport observed.
- Halide migration causes metal electrode degradation, forming $BiBr_x$ species.
- Degradation is observed to initiate from the metal contact edge.
- Ionic barrier layers will be explored in the future to mitigate halide migration to the metal contact.

Acknowledgements

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Thank You