Use of Glow Discharge Optical Emission Spectroscopy to Quantify Thermal Re-distribution of Iodine and Lead in Metal Halide Perovskite Films

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Research Background

Perovskite Solar Cells (PSC) are considered to be the next–generation solar cell technology.

Key Advantages:

- Higher efficiency
- Lower cost
- Easy manufacturing
- Flexibility

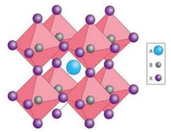


Fig 1: Halide Perovskite Crystal Structure (ABX_3)

Major Challenges: Inherently unstable & degrades faster due to ion migration with light, moisture & heat.

Ion Migration Process in PSC:

- The lattice structure is composed of ions that can move easily.
- In Methyl ammonium Lead Iodide, I^-, MA^+, Pb^{2+} ions migrate when aged under heat.

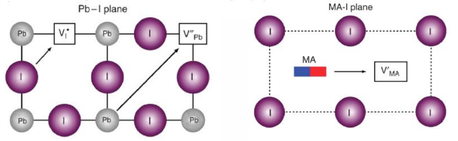


Fig 2: Ion migration in Methyl ammonium Lead Iodide

Advantages of Glow Discharge Optical Emission Spectroscopy (GD-OES)

- Rapid Measurement
- Simple sample preparation

Techniques	Detection Limit (ppm)	Probed Area (Lateral Dia)	Analyzed Depth (nm)	Analysis Time	Vacuum (mbar)
GD-OES	1-100	2-10 mm	From 10 to >150,000	Very fast (s)	10^{-2}
SIMS	10^{-3} -10	1-100 nm	0.01-100	Slow(h)	$<10^{-9}$
SNMS	100	<0.30 mm	0.01-100	Slow(h)	$<10^{-9}$
XPS	100	10-600 µm	<1000	Slow(h)	$<10^{-9}$

Table 1: Comparison of **GD-OES** with different characterization techniques

Research Objective

To observe and quantify ion migration in Methyl ammonium Lead Iodide (MAPI) Perovskite film upon thermal aging by using Glow Discharge Optical Emission Spectroscopy (GD-OES) through elemental depth distribution of the film.

Methodology

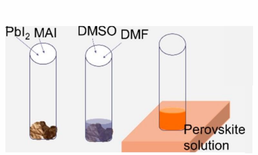
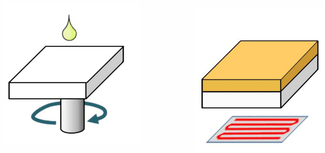


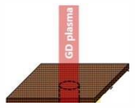
Fig: 4(a)



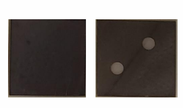
4(b)

4(c)

4(d)



4(e)



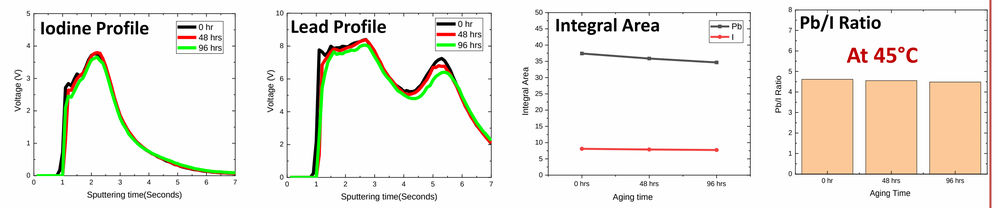
4(f)

4(a): Perovskite Precursor Solution is made with Methyl Ammonium Iodide (MAI) and Lead Iodide (PbI_2) mixed in a solvent of 4:1 Dimethyl Formamide (DMF) and Dimethyl Sulfoxide (DMSO).
4(b): Precursor solution is spun on glass substrate at a speed of 4000 rpm for 30 seconds.
4(c): Annealed at 50 ◦C and then at 100 ◦C for 30 minutes.
4(d): Aging test at 45°C, 65°C and 85°C for 0 hr, 48 hrs and 96 hrs (using glass slide on top).
4(e): Collected data from GD-OES to determine the movement of ions.
4(f): Images of sample before and after GD-OES.

Experiment Results

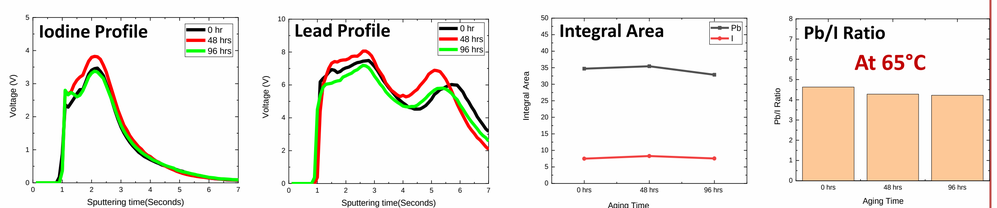
At 45°C

Sample Image(a)



At 65°C

Sample Image(b)



At 85°C

Sample Image(c)

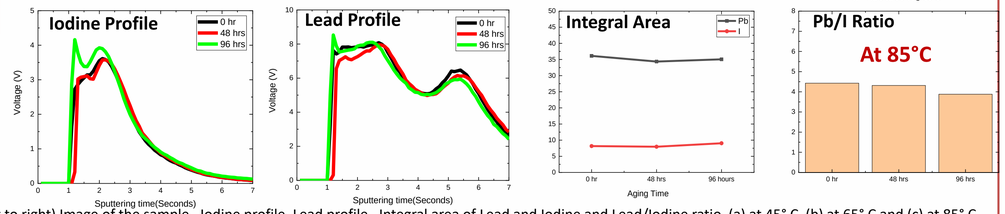


Figure 5: (from left to right) Image of the sample , Iodine profile, Lead profile , Integral area of Lead and Iodine and Lead/Iodine ratio (a) at 45° C (b) at 65° C and (c) at 85° C

Conclusion

We observed that, at 45° C , 65 °C and 85° C, the GD-OES plots (intensity vs. sputtering time) of the Perovskite films are surprisingly quite stable but Pb/I ratio of the MAPI samples decreases with time.

Future Work

- To perform longer exposures of heat and cross-correlate against other characterization techniques to quantify degradation that occurs in the MHP films.
- Study other perovskite compositions (such as $CsPbI_3$ and $CsFAPbI_3$) to see if those compositions hold a similar trend for aging.

Acknowledgement and References:

I would like to acknowledge Dr. Nicholas Rolston for his valuable guidance, Vineeth Penukula for his mentorship and all the members in the Rolston lab for their commendable support throughout my project. My gratitude to MORE program at Arizona State University and Intel for giving me the opportunity to pursue my research project.

1.Zheng, D., Volovitch, P., & Pauporté, T. (2022). What Can Glow Discharge Optical Emission Spectroscopy (GD-OES) Technique Tell Us about Perovskite Solar Cells?. *Small methods*, *6*(11), e2200633. https://doi.org/10.1002/smtd.202200633
2.Islam MA, Mohafez H, Sobayel K, Wan Muhamad Hatta SF, Hasan AKM, Khandaker MU, Akhtaruzzaman M, Muhammad G, Amin N. Degradation of Perovskite Thin Films and Solar Cells with Candle Soot C/Ag Electrode Exposed in a Control Ambient. *Nanomaterials*. 2021; 11(12):3463. https://doi.org/10.3390/nano11123463
3.Enbing Bi, Zhaoning Song,Chongwen Li,Zhifang Wu,and Yanfa Yan - Mitigating ion migration in perovskite solar cells - Trends in Chemistry, July 2021, Vol. 3, No. 7 https://doi.org/10.1016/j.trechm.2021.04.004.

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