Self-doping in high-band gap perovskite films

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Abstract

We address the question "HOW DO DIFFERENT CATIONS & ANIONS AFFECT CARRIER' DIFFUSION LENGTHS and JUNCTION FORMATION in HIGH BANDGAP HALIDE PEROVSKITE (HaP) FILM-based SOLAR CELLS ?" Such HaP films are of interest for solar spectrum splitting and driving photo-electrochemical reactions for fuel production. Resolving how the addition of cations and anions change the (unintentional) doping of the HaP is critical for basic understanding of film and device physics, as well as for improving device performance.

We studied HaP films with the general formula $APbX_3$, where A can be a mixture of formamidinium (FA), methylammonium (MA) and cesium (Cs) and X can be a mixture of bromine and chlorine by combining several techniques:

- Dark-conductivity and Photo-conductivity, - Electron Beam-Induced Current, EBIC, and - Steady-State Photocarrier-Grating (SSPG).

Stand-alone Thin films – Resistivity Measurements

	$MAPbBr_{3-x}Cl_x$	$MAPbBr_3$	$CsPbBr_3$	$FAMACsPbBr_3$
Dark **Resistivity** [MΩ·cm]	0.004±0.002	44±5	0.004±0.002	180±80
Hole Concentration* [cm^{-3}]	**3±2 X 10^{13}**	**2.8±0.3 X 10^{9}**	**3±2 X 10^{13}**	**7±3 X 10^{8}**

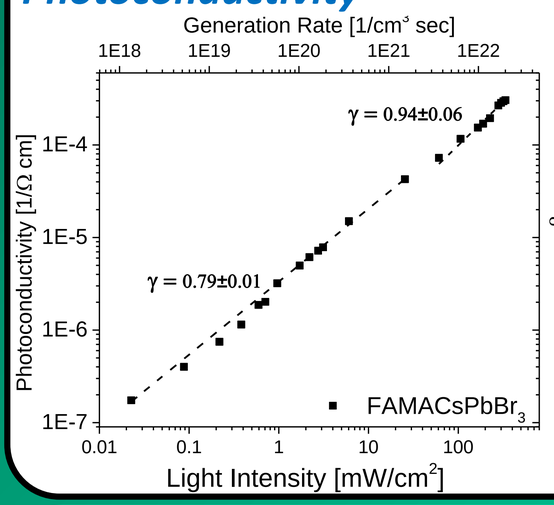
$$\sigma_{dark} = q \cdot \mu \cdot p$$

Our $MAPbBr_{3-x}Cl_x$ and $CsPbBr_3$ layers are significantly higher doped than $MAPbBr_3$ and $FAMACsPbBr_3$ ones.

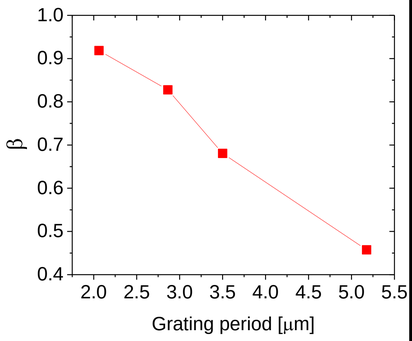
*Estimated using μ= 50 cm^2/Vsec, from our photo-Hall measurements ; assuming that all the dopants are ionized

Extracting carrier diffusion lengths for $FAMACsPbBr_3$

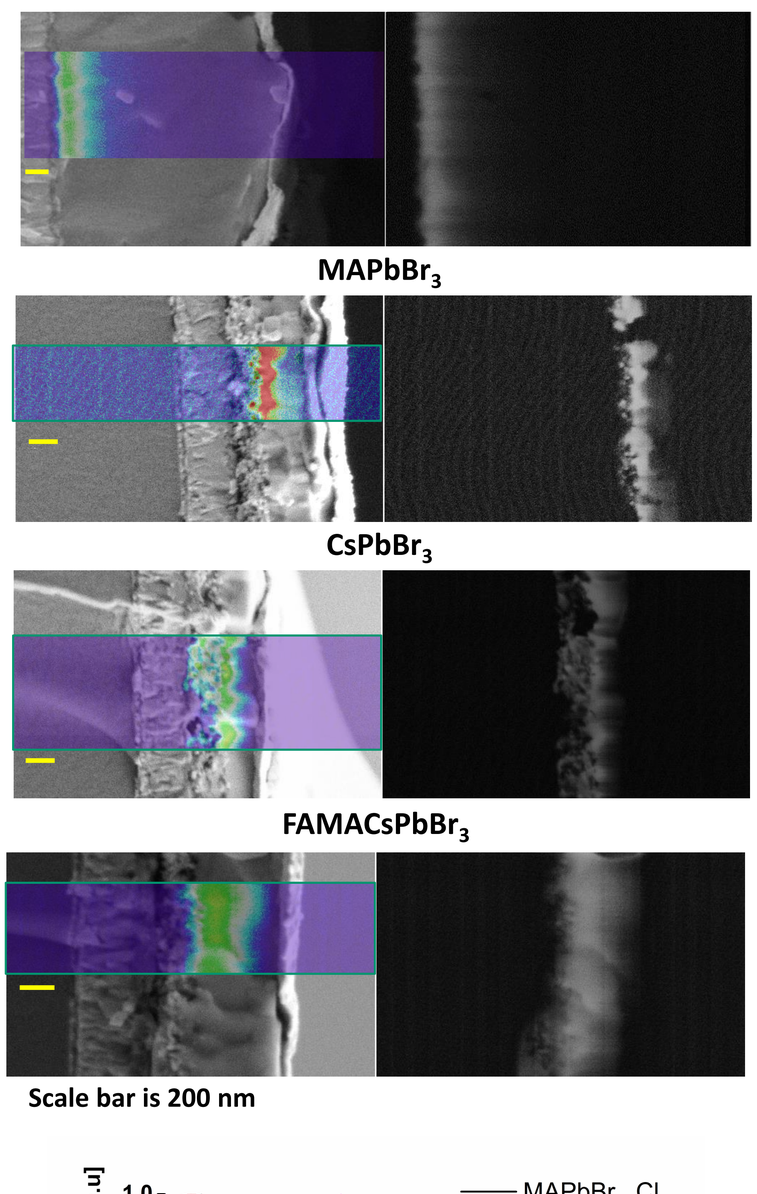
Photoconductivity



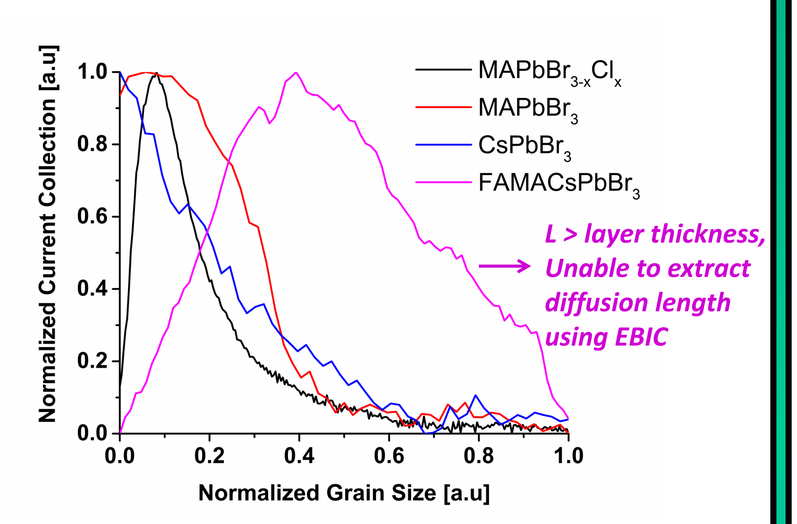
SSPG



Junction type and carrier diffusion lengths from EBIC

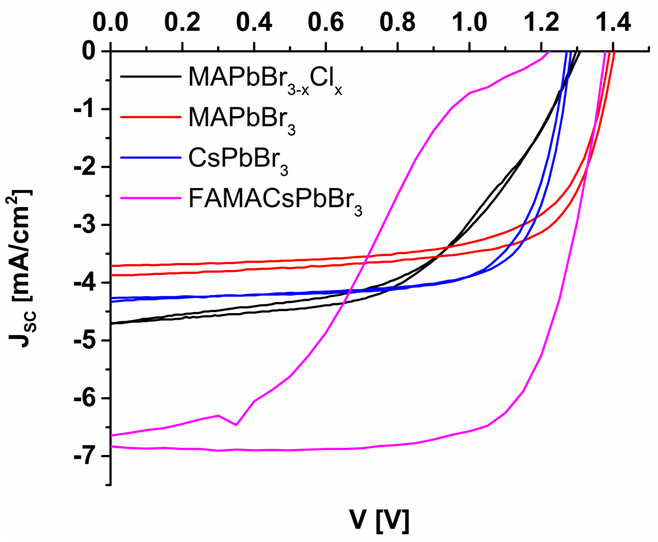


Scale bar is 200 nm



$FAMACsPbBr_3$ forms a junction resembling a p-i-n junction while with the other films a p-n junction forms

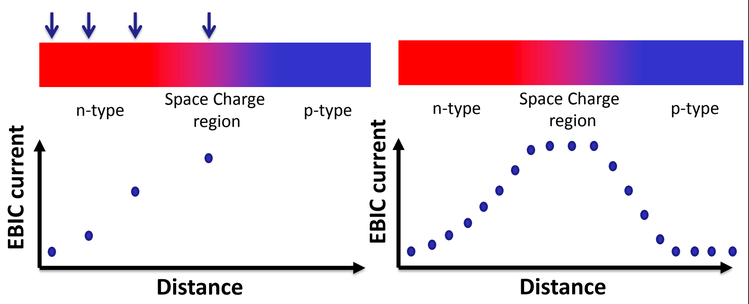
Solar cell device characteristics



Unlike the single cation devices, $FAMACsPbBr_3$ has a strong hysteresis in the device I-V characteristics

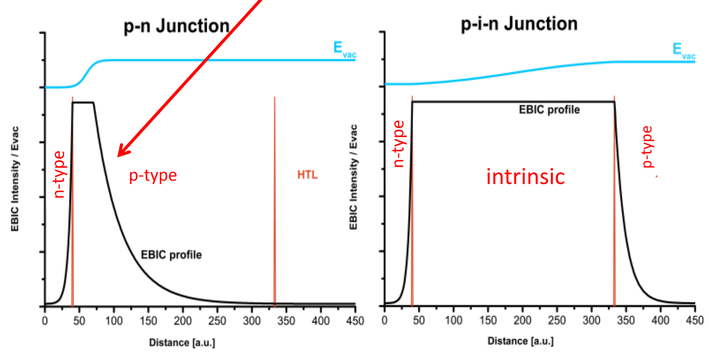
Film Type	Diffusion Length [nm]
black: dark **$MAPbBr_{3-x}Cl_x$**	50±15 (e^-) [EBIC]
$MAPbBr_3$	60±15 (e^-) [EBIC]
$CsPbBr_3$	77±15 (e^-) [EBIC]
red: illuminated **$FAMACsPbBr_3$**	**640±100 (e^-), 990±150 (h^+)** [SSPG+PC]
$MAPbBr_{3-x}Cl_x$	360±22 (e^-) [EBIC]

From EBIC Profile to Working Mechanism



Mono-exponential decay

$$y = y_0 + Ae^{\left(\frac{x_0 - x}{L_n}\right)}$$



Conclusions and open question

- From dark resistivity measurements, $MAPbBr_3$ and $FAMACsPbBr_3$ seem to be much more intrinsic than $MAPbBr_{3-x}Cl_x$ and $CsPbBr_3$.
- Although the doping in $MAPbBr_3$ and $FAMACsPbBr_3$ films is similar, the charge carrier diffusion lengths in $FAMACsPbBr_3$ are significantly larger than in $MAPbBr_3$.
- $FAMACsPbBr_3$ films seem to be ambipolar with diffusion lengths, **similar to $MAPbI_3$.**
- Could the significant hysteresis observed in cells with $FAMACsPbBr_3$ layers be due to its ambipolar nature ***or*** to the increased number of cation species present, which enhance ion migration?

Acknowledgements

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