Passivation of grain boundaries and chemical stability in organic-inorganic lead halide perovskite solar cells

Gee Yeong Kim, Bich Phuong Nguyen, and William Jo

Department of Physics, Ewha Womans University, Seoul, Korea

(*wmjo@ewha.ac.kr)

Outline

➢ Introduction

- Current Issues in Thin-Film Solar Cells and Emerging Energy Materials

➢ Results & Discussion

- Passivation of grain-boundaries with organic-inorganic perovskite lead halides
- Chemical stability in organic-inorganic perovskite lead halides

➢ Summary

William Jo's laboratory at Ewha W. Univ.

- **Professor :** **William Jo**
- **Graduate students** : **Gee Yeong Kim (post-doc MPI-Stuttgart),** Seol Hee Oh, Hyejin Jin, Bich Phuong Nguyen, Jihye Kim, Juran Kim, Hye Ri Jung, and Hoa Thi Dao
- **Research topics** : Thin-film solar cells, Oxides, and 2D materials

Lab Facilities and Instruments

Fabrication

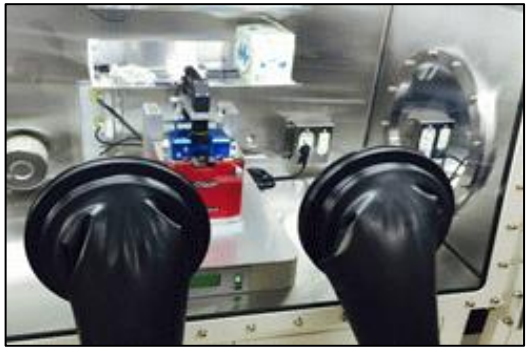
- E-beam and thermal deposition
- Spin coating w/ glove box
- Chemical bath deposition
- Chemical vapor deposition

E-beam & thermal evaporator

Chemical vapor deposition

Characterization

- Kelvin probe force microscopy
- Conductive atomic force microscopy
- Scanning electron microscopy
- Energy dispersive X-ray spectroscopy
- X-ray diffraction
- Solar simulator
- UV-Vis spectroscopy

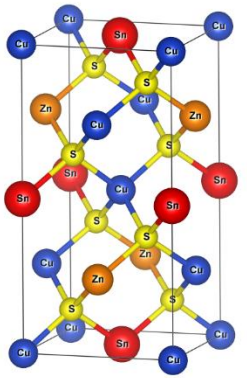


Glove box AFM

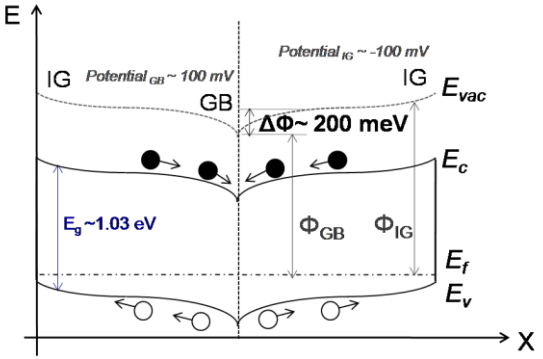
Solar simulator (I-V and C-V)

Materials for solar cell applications and analysis

- **Fabrication of new materials and concepts for PV devices**
  - $Cu_2Zn(Sn,Ge)(S,Se)_4$, $Cu(In,Ga)Se_2$
  - Organic-inorganic halide perovskite solar cells: $CH_3NH_3MX_3$ (M=Pb or Sn, X=Cl, I, or Br)
  - New emerging materials for energy conversion: FeS_2, SnS_2



- **Advanced characterization of physical and material properties**
  - Identification of phases of thin-films (microscale, nanoscale)
  - Electrical properties of grain boundary
  - Device properties of solar cells
  - Optical properties of materials for solar cell applications
  - Characterization of structural, electrical, and optical properties of absorber layers for solar cells



Publications (2014-2016)

Kesterite : 10 papers, 1 under review , 1 in preparation

[12] G. Y. Kim *et al.* "Sodium Mediated Passivation of Grain Boundaries on $Cu_2ZnSnSe_4$: Nanometer-scale Mapping of Surface Potential", *Chemistry of Materials* (to be submitted).

[11] Juran Kim *et al.* "Influence of Na diffusion induced by Mo back-contact annealing on surface potential and carrier transport in Cu_2ZnSnS_4 thin film solar cells", *Solar Energy Materials and Solar Cells (submitted).*

[10] G. Y. Kim *et al.* "Enhancement of photo-conversion efficiency in $Cu_2ZnSn(S,Se)_4$ thin-film solar cells by control of ZnS precursor-layer thickness", *Progress in Photovoltaics: Research and Applications* **24**, 292 (2016).

[9] S. -N. Park *et al.* "Nanostructured p-type CZTS thin films prepared by facile solution process for 3D p-n junction solar cells", *Nanoscale* **7**, 11182 (2015).

[8] K. -J. Yang, *et al.* "Effects of the compositional ratio distribution with sulfurization temperatures in the absorber layer on the defect and surface electrical characteristics of Cu_2ZnSnS_4 solar cells", *Progress in Photovoltaics: Research and Applications* **23**, 1771 (2015).

[7] G. Y. Kim *et al.* "Optical and surface probe investigation of secondary phases in Cu_2ZnSnS_4 films grown by electrochemical deposition", *Solar Energy Materials and Solar Cells* 139, 10 (2015).

[6] T. T. T. Nguyen, *et al.* "Raman scattering studies of Cu_2ZnSnS_4 thin films: Local distribution of the secondary phase $Cu_{2-x}S$ and the effect of KCN etching on $Cu_{2-x}S$", *Journal of the Korean Physical Society* **66**, 117 (2015).

[5] G. Y. Kim *et al.* "Effects of $Cu_{2-x}S$ phase removal on surface potential of Cu_2ZnSnS_4 thin-films grown by electroplating", *Current Applied Physics* **14**, 1665 (2014).

[4] G. Y. Kim *et al.* "Nanoscale investigation of surface potential distribution of $Cu_2ZnSn(S,Se)_4$ thin films grown with additional NaF layers", *Nano Convergence* **1**, 27 (2014).

[3] G. Y. Kim *et al.* "Surface potential on grain boundaries and intra grains of highly efficient $Cu_2ZnSn(S,Se)_4$ thin-films grown by two-step sputtering process", *Solar Energy Materials and Solar Cells* **127**, 129 (2014).

[2] D. Nam, G. Y. Kim, *et al.* "Composition variations in $Cu_2ZnSnSe_4$ thin films analyzed by XRD, EDS, PIXE, PL and Raman Spectroscopy", *Thin Solid Films* **562**, 109 (2014).

[1] G. Y. Kim *et al.* "Nanoscale observation of surface potential and carrier transport in $Cu_2ZnSn(S,Se)_4$ thin-films grown by sputtering-based two-step process", *Nanoscale Research Letters* **9**, 10 (2014).

Chalcopyrite : 3 papers,

Gee Yeong Kim

[4] G. Y. Kim, J. Y. Yang, T. T. T. Nguye
Jeon, J. Nam, D. Lee, D. Kim, Y. –K. Ki
photo-conversion efficiency in double-g
film solar cells with two-step sulfurization
Photovoltaics: Research and Application

[3] J. Y. Yang, J. Nam, D. Kim, G. Y. Kim
"Enhancement of the photo c
$Cu(In,Ga)(Se,S)_2$ solar cells fabricate
process", *Applied Physics Letters* **107**, 1

[2] G. Y. Kim, W. Jo, H.-J. Jo, D.-H. Kim, and J.-K. Kang
"Macroscopic and microscopic electrical
thin-film solar cells with various Ga/(In+Ga) contents", *Current Applied Physics* **15**, S44 (2015).

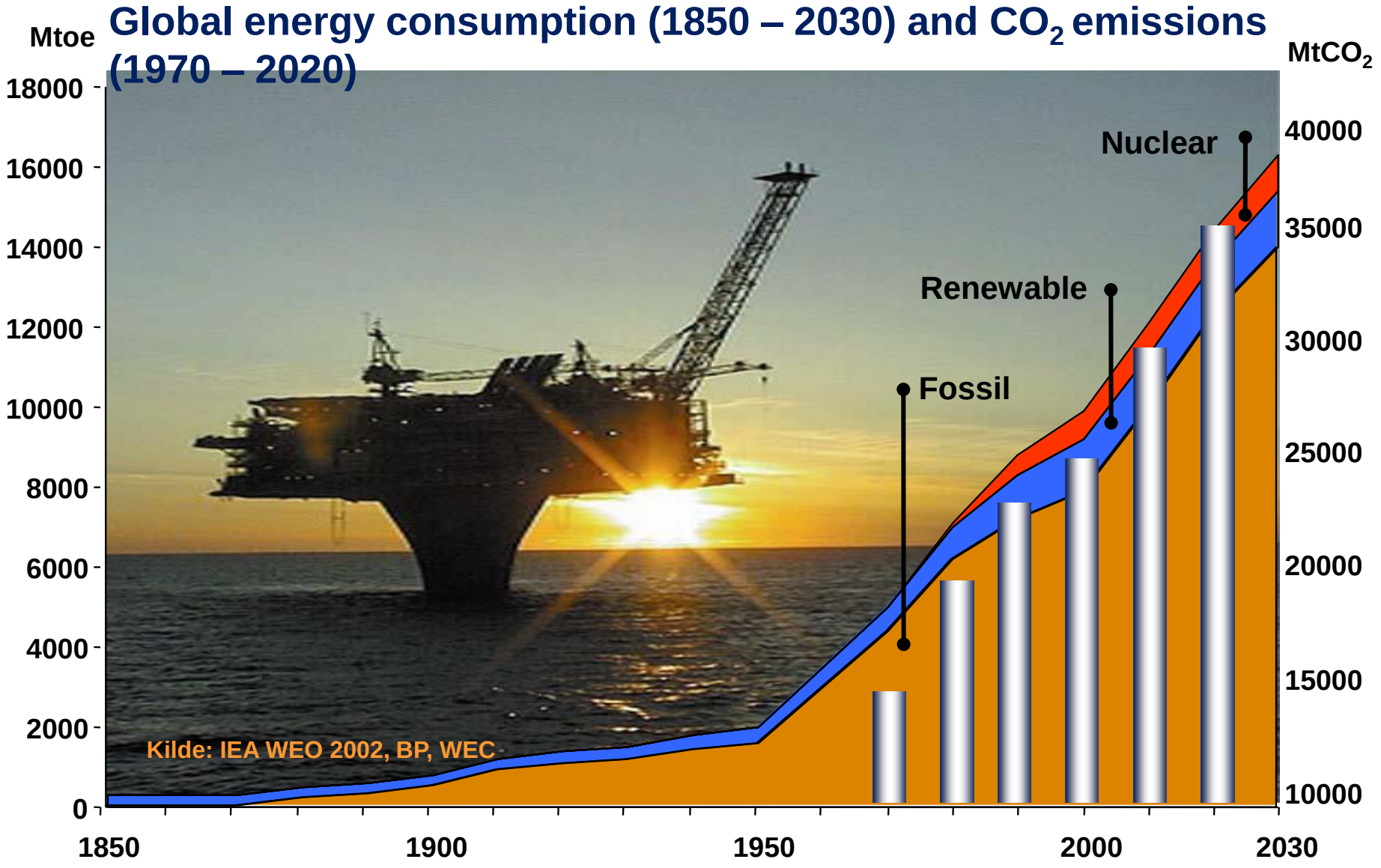
[1] J. Y. Yang, D. Lee, K. S. Huh, S. J. Jung, J. W. Lee, H. C. Lee, D. H. Baek, B. J. Kim, D. Kim, J. Nam, G. Y. Kim, and W. Jo, "Influence of surface properties on the performance of $Cu(In,Ga)(S,Se)_2$ thin film solar cells using Kelvin probe force microscopy", *RSC Advances* **5**, 40719 (2015).

Perovskite : 1 paper, 1 under review

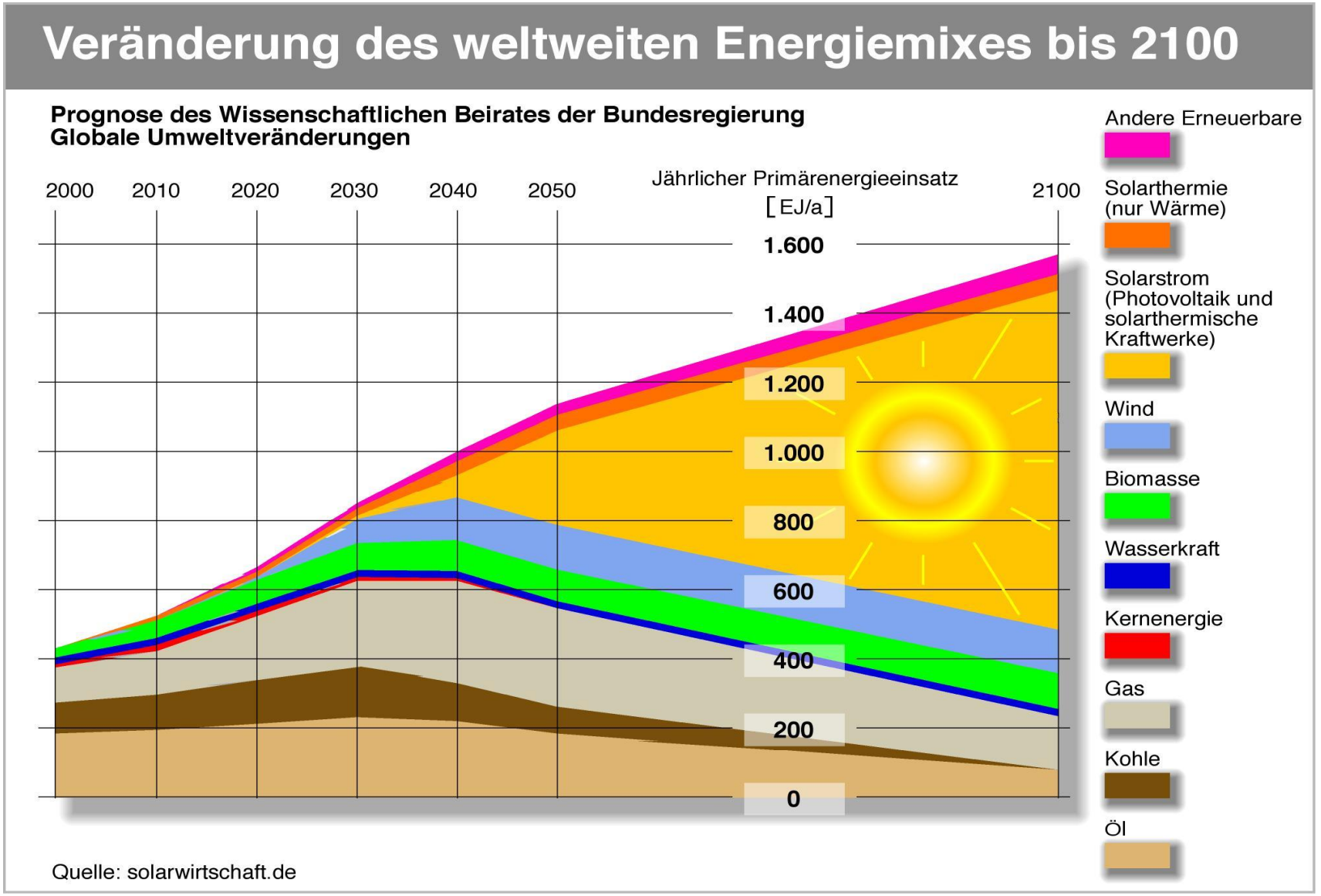
[2] B. P. Nguyen, G. Y. Kim, W. Jo, B. J. Kim, and H. S. Jung, "Chemical stability of $CH_3NH_3Pb(I,Br)_3$ mesoporous perovskite solar cells probed by surface potential and carrier transport", *Journal of Physical Chemistry-C* (submitted).

[1] G. Y. Kim, S. H. Oh, B. P. Nguyen, W. Jo, B. J. Kim, D. G. Lee, and H. S. Jung, "Efficient Carrier Separation and Intriguing Switching of Bound Charges in Inorganic−Organic Lead Halide Solar Cells", *Journal of Physical Chemistry Letters* **6**, 2355 (2015).

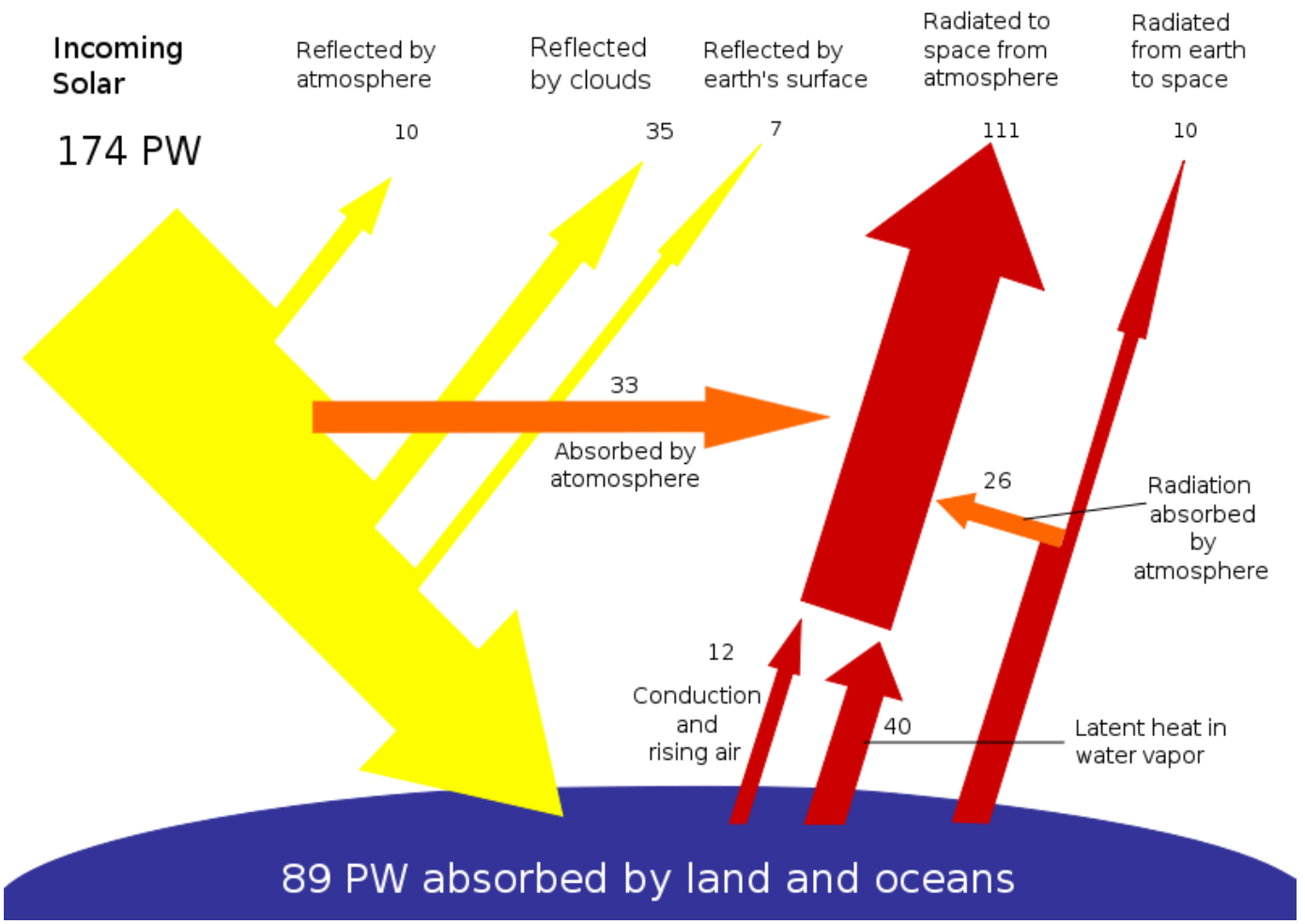
The need for renewable energy



Future energy



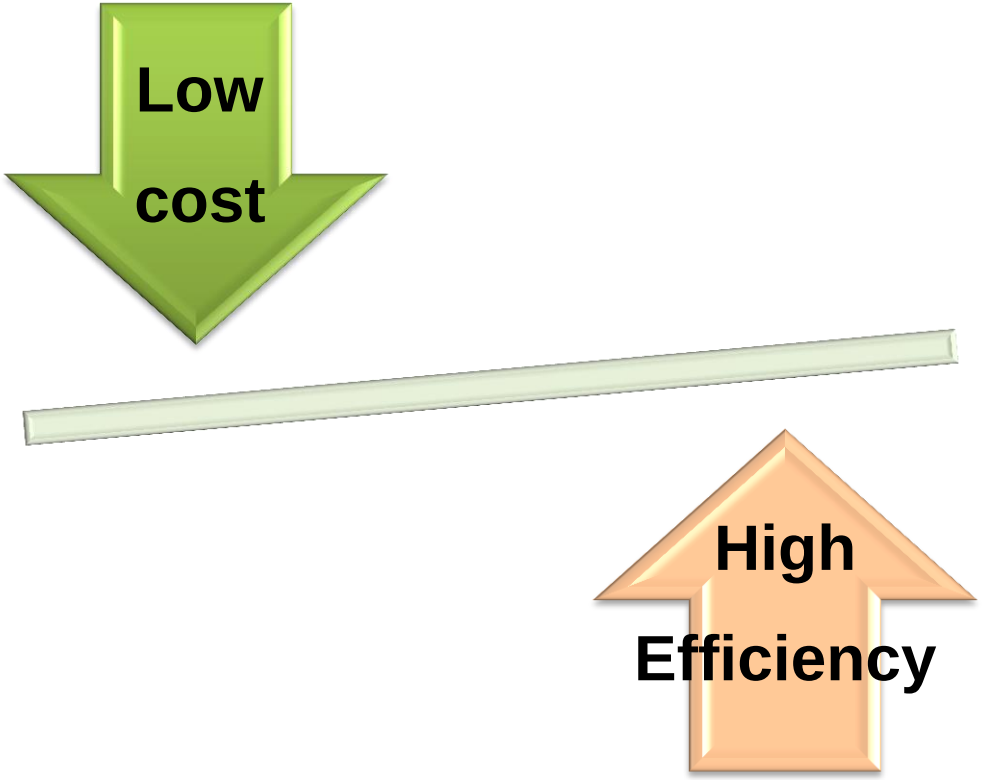
Solar energy



80,000 terawatts of solar power fall on the earth constantly, compared to 14.5 terawatts current used for human power.

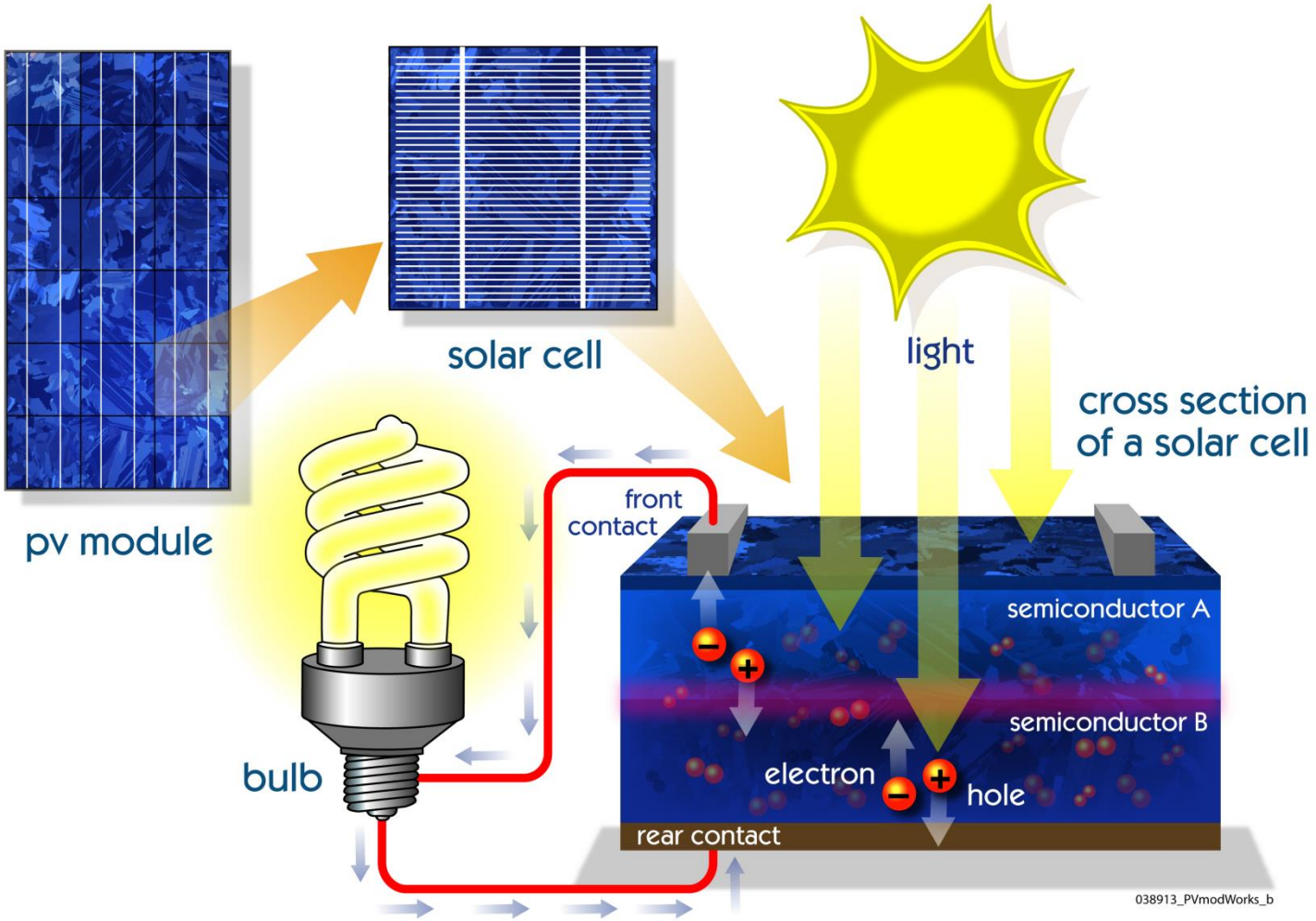
Solar cell research

The goal of solar cell research

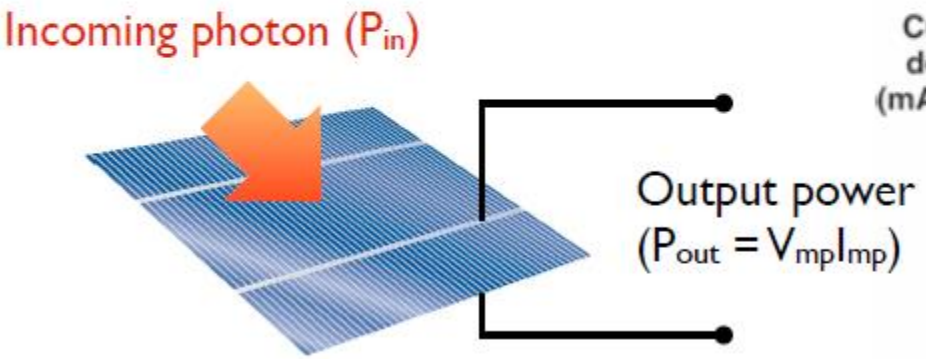


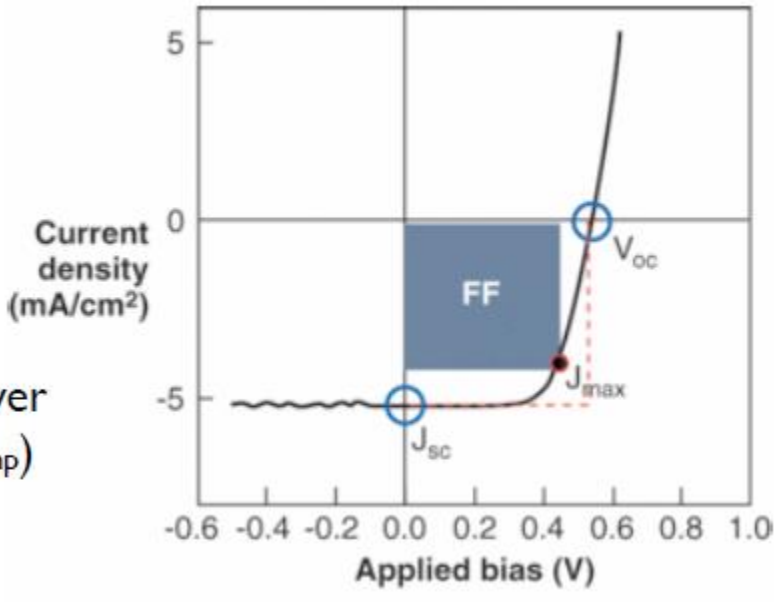
Principle of solar cells

Photovoltaics



Solar cell efficiency



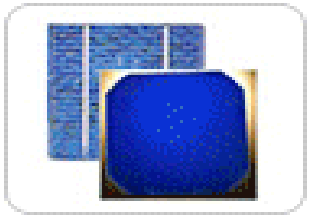


Energy conversion efficiency

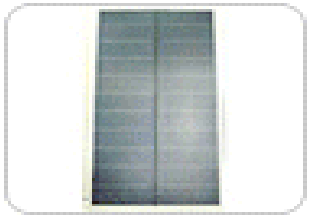
$$\eta = \frac{V_{mp} I_{mp}}{P_{in}} = \frac{V_{oc} I_{sc} FF}{P_{in}}$$

Classification of solar cells

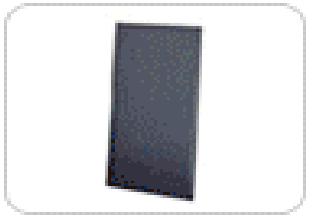
Solar cells	Si	Crystalline Si	Single Crystalline	Commercialization
			Poly-Crystalline	Mass production
		Amorphous Si		R&D
	Compound Semiconductors	II-VI	CdTe	Commercialization / Mass production
			$Cu(In,Ga)Se_2$	
			$Cu_2ZnSnSe_4$	R&D
		III-V	GaAs	Manufacture
			InP	
			InGaAs	
		Emerging	Quantum dot	R&D
			Dye cell	
			Perovskites	



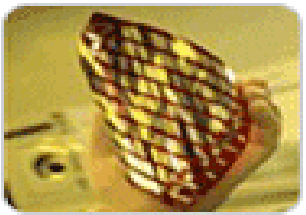
Single/Poly Si



Si thin-films



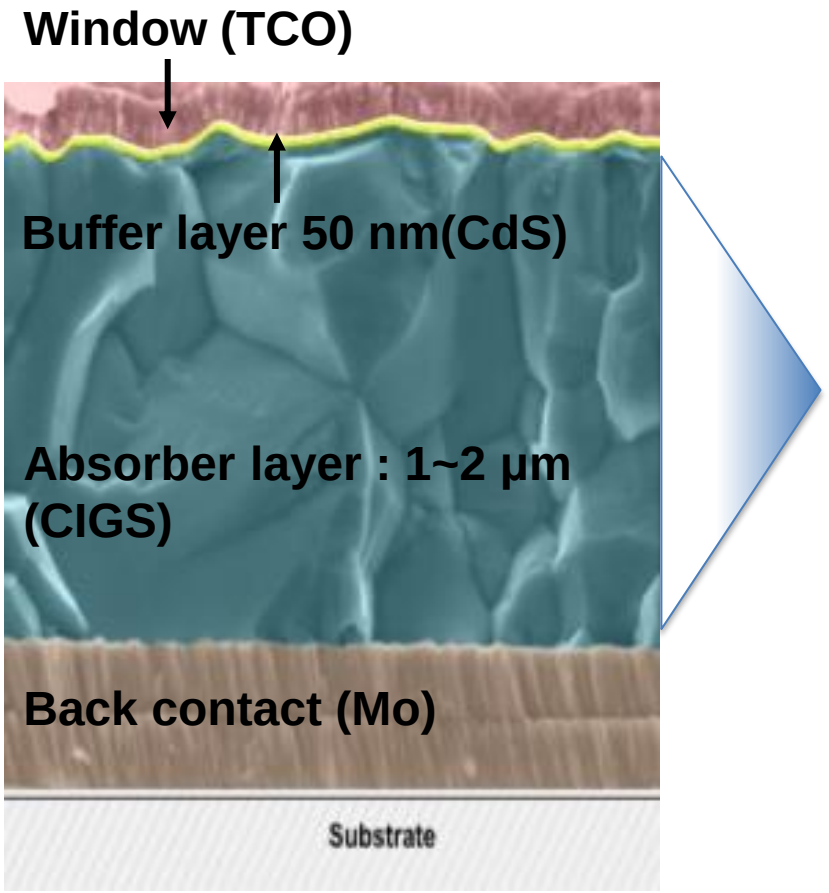
CIS films



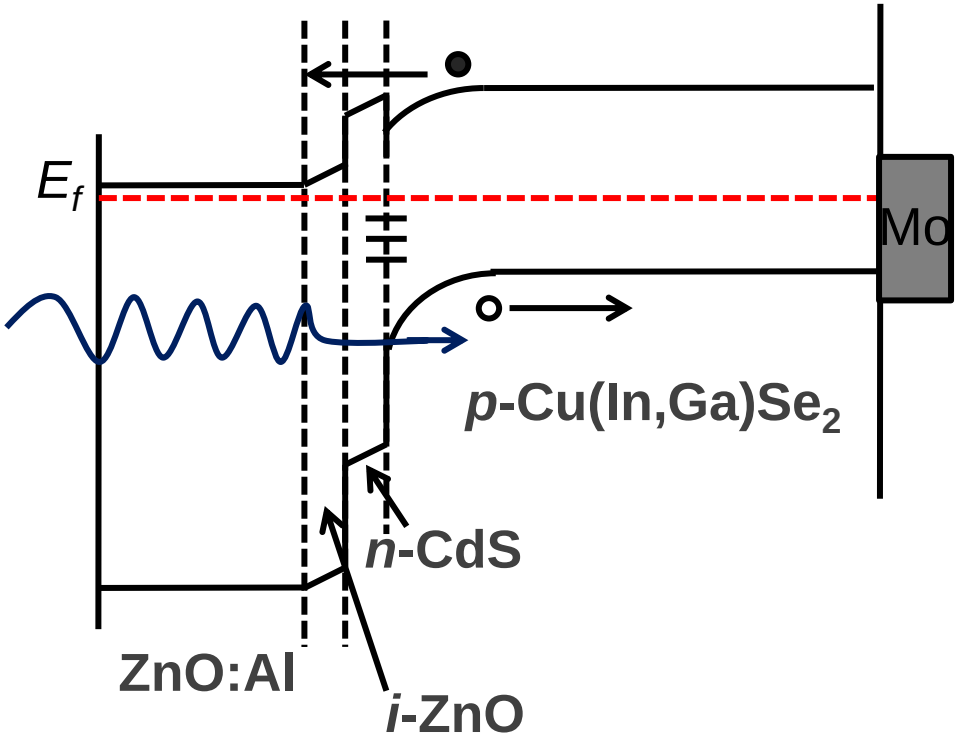
Flexible solar cells

Structure of $CuInGaSe_2$ thin-film solar cells

CIGS thin-film solar cell

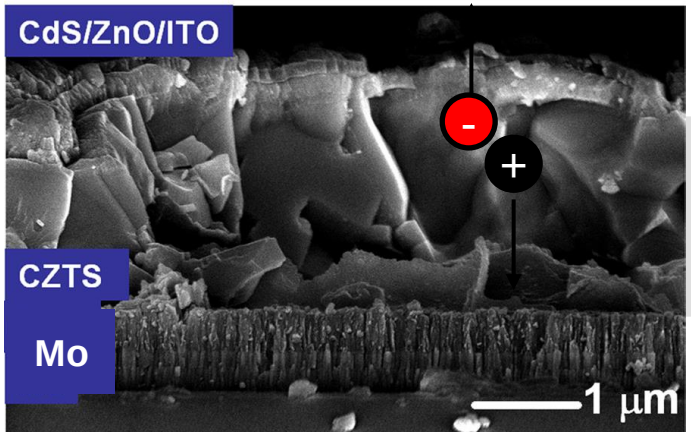


Band structure of CIGS thin-film solar cell



Structure and advantages of $Cu_2ZnSn(S,Se)_4$

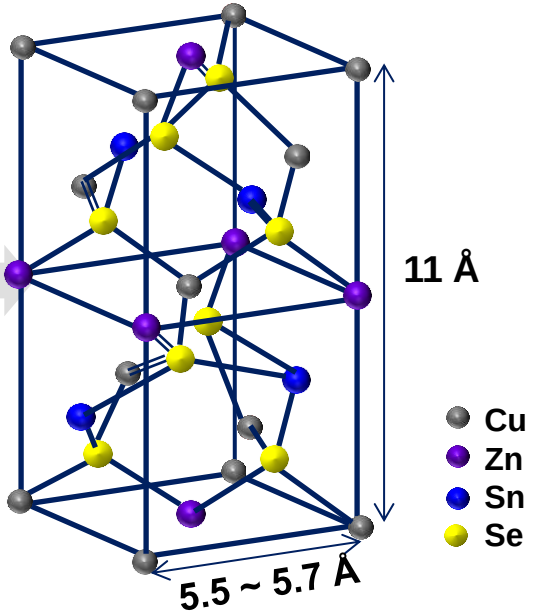
$Cu_2ZnSn(S,Se)_4$ (CZTSSe) solar cell structure



Ahmed *et al.* Adv. Energy Mater. **2** (2012) 253.

Crystal structure

Kesterite



Space group : $I\bar{4}$

Advantages

- **Low cost material**

- CIGS : 1 $/$W_p$
- CZTS : 0.75 $/$W_p$

- **High absorption coefficient** (a few μm)

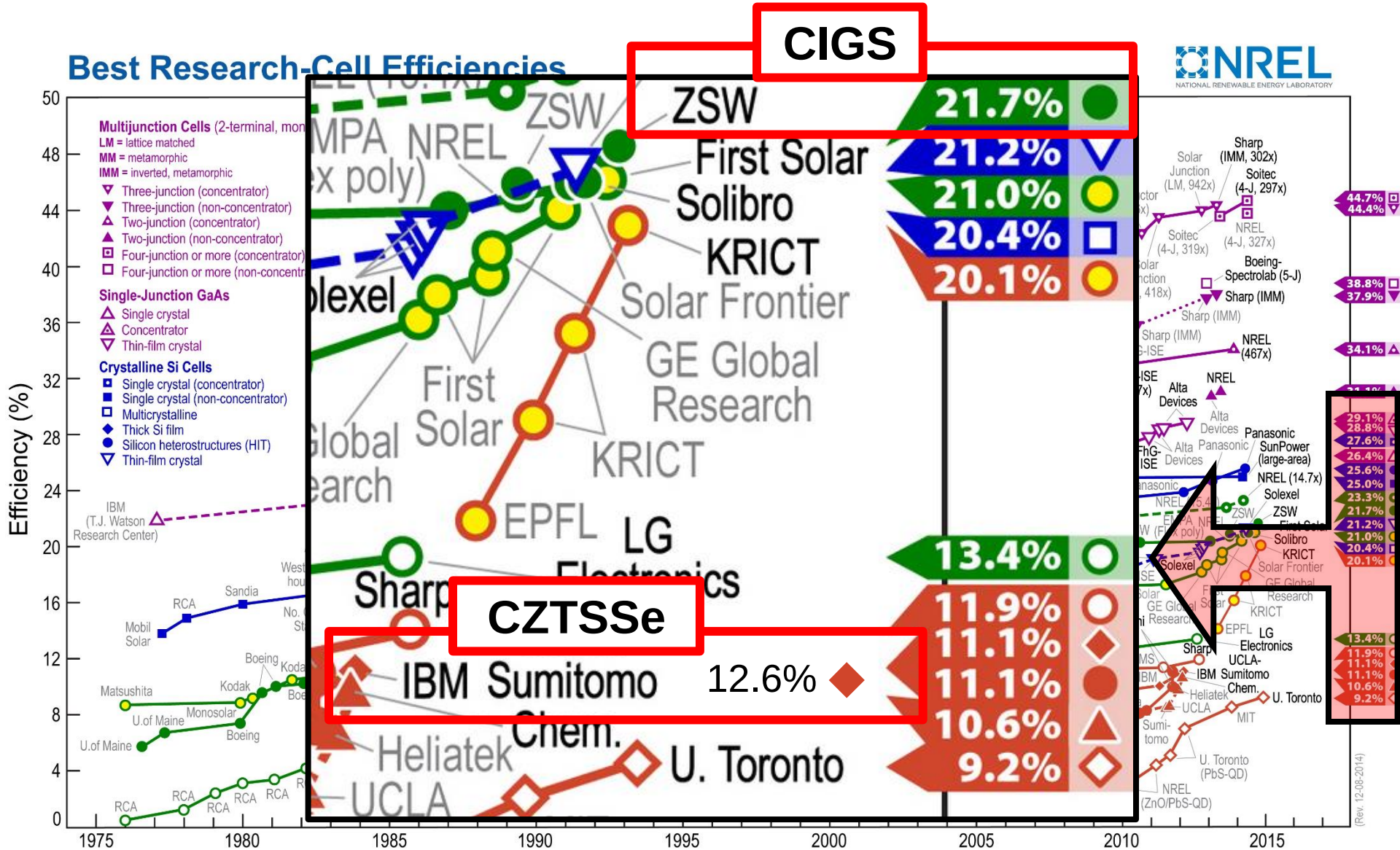
- Si > 0.01 cm^{-1}
- CZTS > 10^4 cm^{-1}

- **Optimal band gap**

- 1.0 ~ 1.5 eV

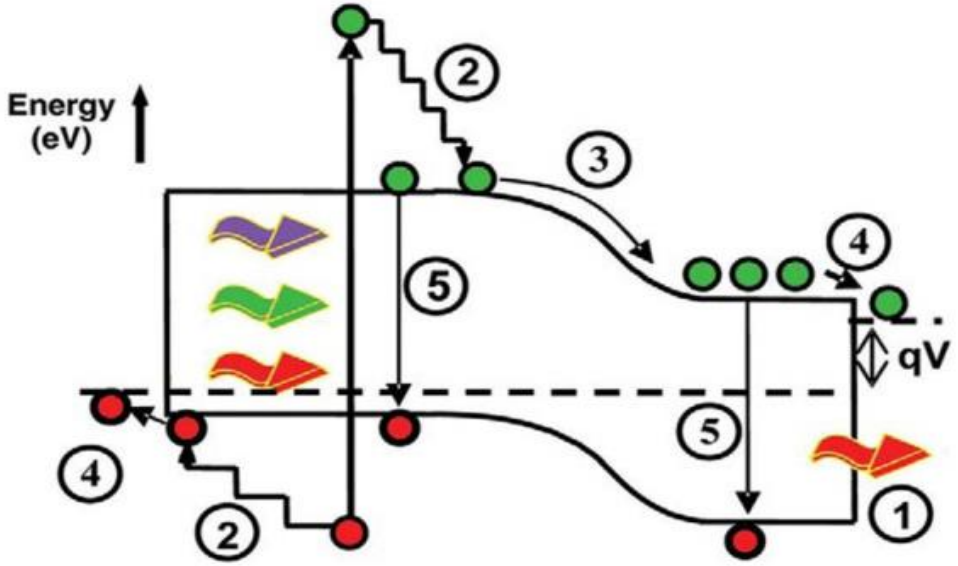
- **Band gap can tune by S/Se**

Recent record solar cell efficiencies



Efficiency loss in thin-film solar cell

Energy loss of solar cell



(1) Unabsorbed light

(2) Excess energy loss as heat

(3) Fermi level mismatch with band gap

(4) Transfer loss

(5) <u>Electron-hole recombination loss</u> **→ Grain boundary (GB) issue !**

THE JOURNAL OF PHYSICAL CHEMISTRY Letters

Letter

pubs.acs.org/JPCL

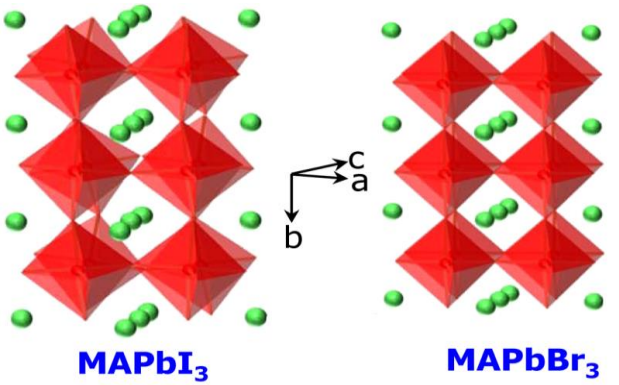
Efficient Carrier Separation and Intriguing Switching of Bound Charges in Inorganic–Organic Lead Halide Solar Cells

Gee Yeong Kim,[†] Seol Hee Oh,[†] Bich Phuong Nguyen,[†] William Jo,*[,†] Byeong Jo Kim,[‡] Dong Geon Lee,[‡] and Hyun Suk Jung[‡]

[†]Department of Physics, Ewha Womans University, Seoul 120-750, South Korea

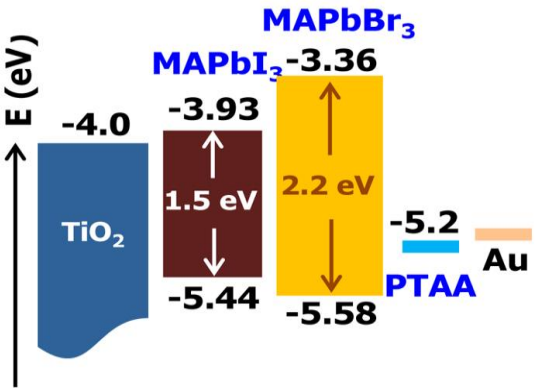
[‡]School of Advanced Materials Science & Engineering, Sungkyunkwan University, Suwon 440-746, Korea

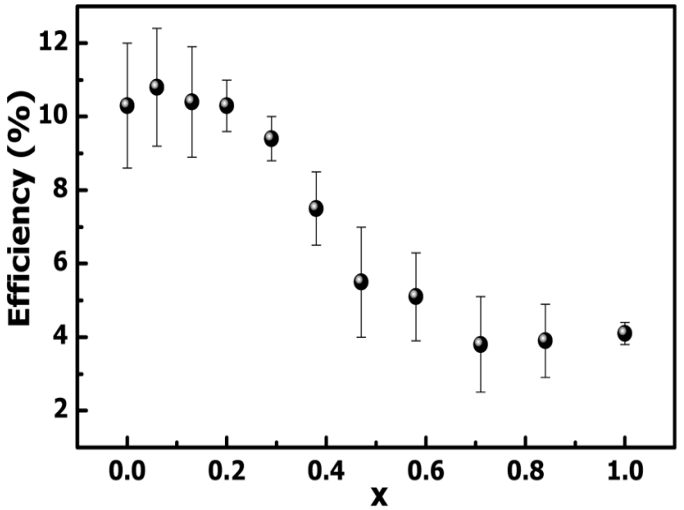
$CH_3NH_3Pb(I_{1-x}Br_x)_3$ perovskite solar cells



(Tetragonal I4/mcm)
But, centrosymmetric

(Cubic Pm3m)

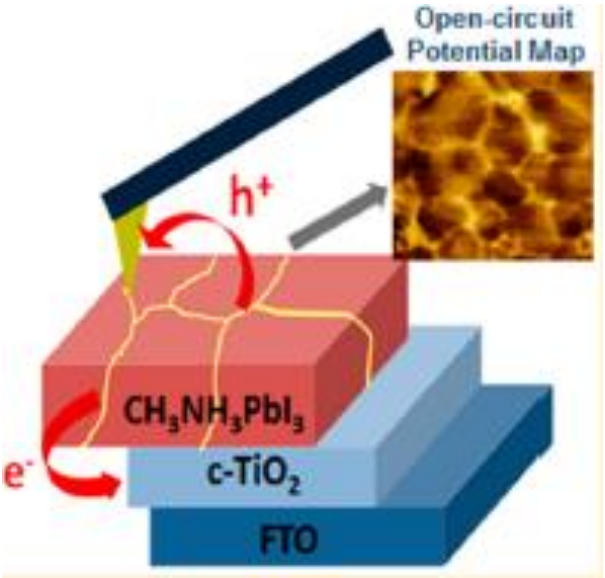




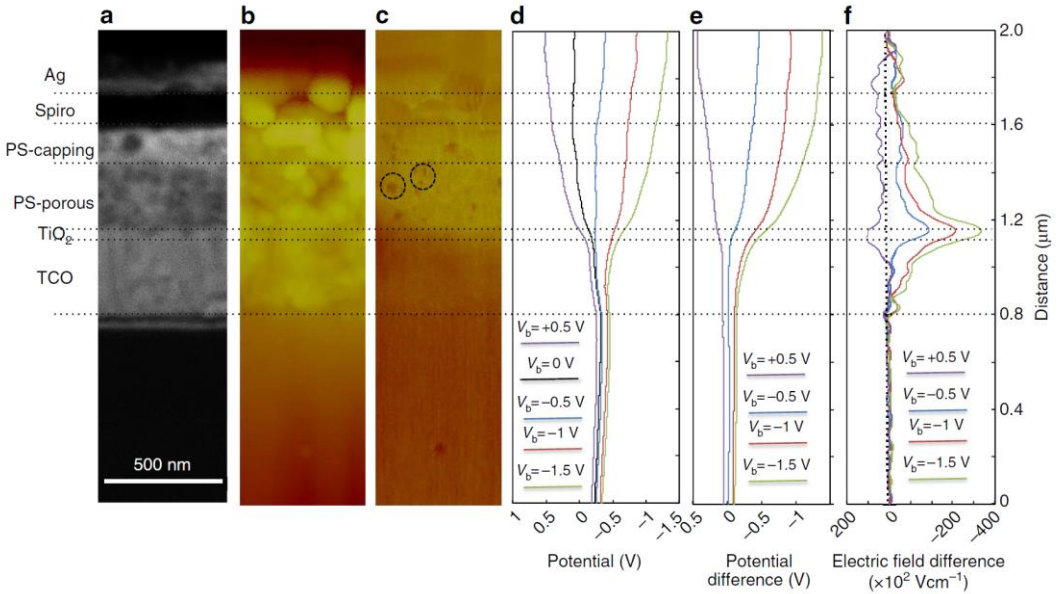
Noh and Seok *et al*. Nano. Lett. **13** (2013) 1764

- Change of $CH_3NH_3Pb(I_{1-x}Br_x)_3$ bandgap by Br concentration (1.57-2.29 eV)

Kelvin probe microscopy studies in perovskite solar cells



J. S. Yun *et al*. J. Phys. Chem. Lett. **6** (2015) 875-880

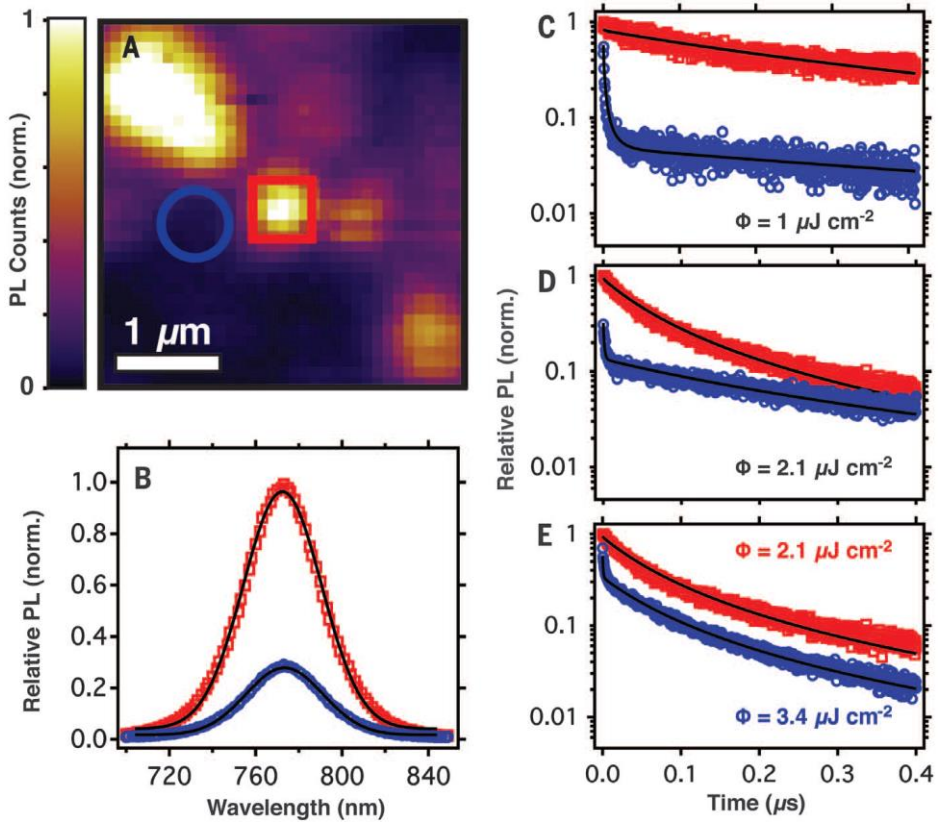


C. S. Jiang *et al.* Nature Comm. **6** (2015) 8397

- GBs in planar perovskite solar cells present beneficial effects of efficient charge separation and collection.
- Determination of device operation for power output based on p–n junction structure and the minority-carrier diffusion/drift operation, rather than the mechanism of exciton separation

Local fluorescence lifetime at GBs in perovskite solar cells

Fluorescence microscopy of $CH_3NH_3PbI_3(Cl)$ film and local PL measurements

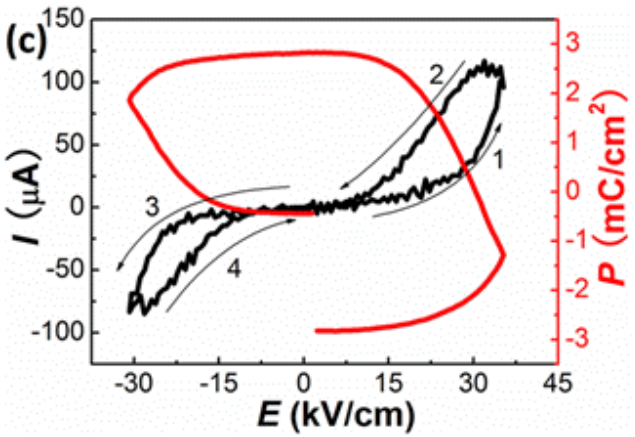


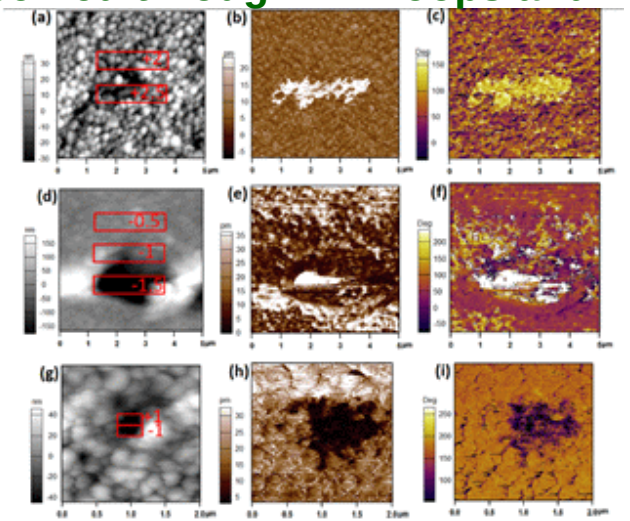
D. W. deQuilettes *et al*. Science **348** (2015) 683

- PL intensities and lifetimes varied between different grains and GBs in the same film, even for films established long lifetimes.
- GBs in $CH_3NH_3PbI_3(Cl)$ film shows lower PL intensity and shorter local PL lifetime than grains.

Ferroelectricity of $CH_3NH_3PbI_3$ perovskite ?

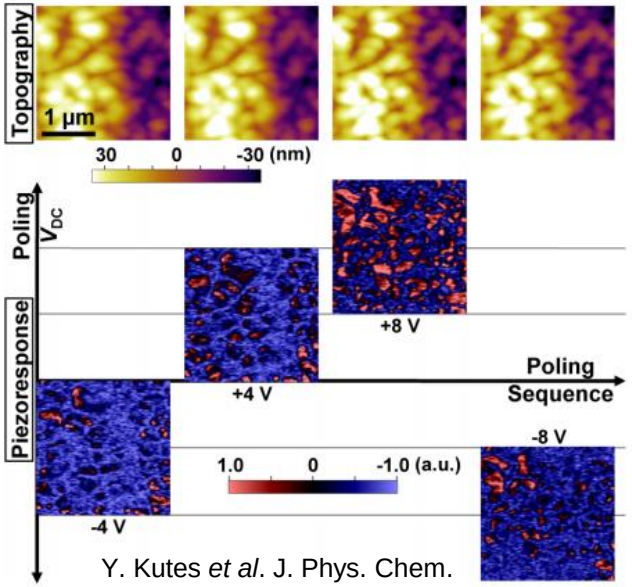
No ferroelectric behavior is observed through P-E loops and PFM



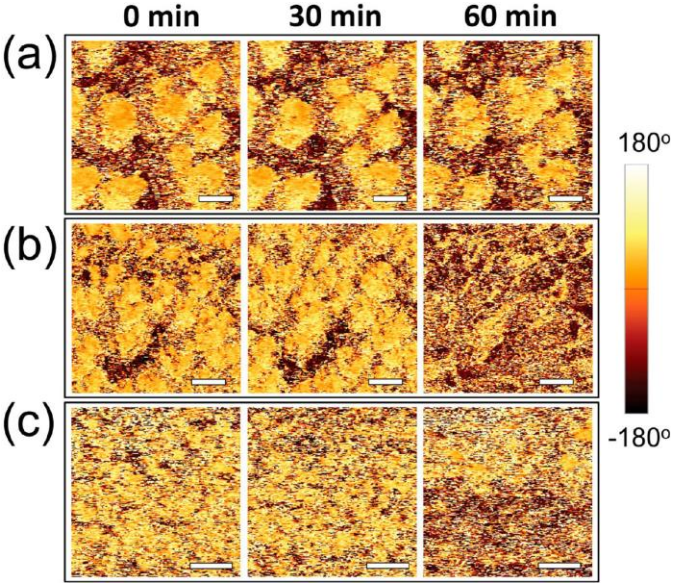


Z. Fan *et al*. J. Phys. Chem. Lett.**6** (2015) 1155

Ferroelectric polarization behavior and ferroelectric domains in $CH_3NH_3PbI_3$



Y. Kutes *et al*. J. Phys. Chem. Lett.**5** (2015) 3335

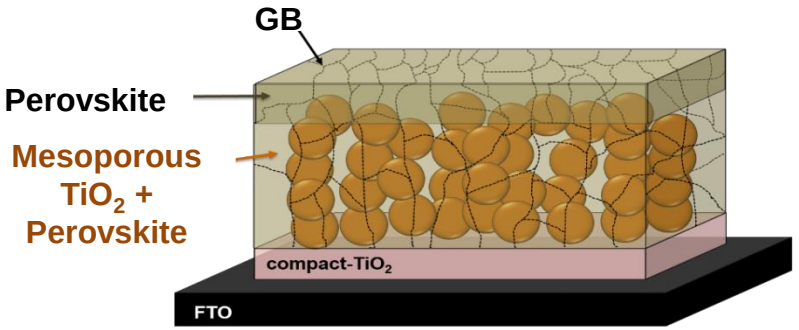


H. –S. Kim *et al*. J. Phys. Chem. Lett.**6** (2015) 1729

Growth and characterization of $CH_3NH_3Pb(I,Br)_3$

- **Spin coating and materials for perovskite solar cells**

- Spin coating (glove box, N_2 environment)
- FTO/compact-TiO_2/meso-TiO_2/$CH_3NH_3Pb(I,Br)_3$ (control of Br concentration)
- Device: Hole transport layer: spiro-MeOTAD, Ag electrode (thermal evaporation)

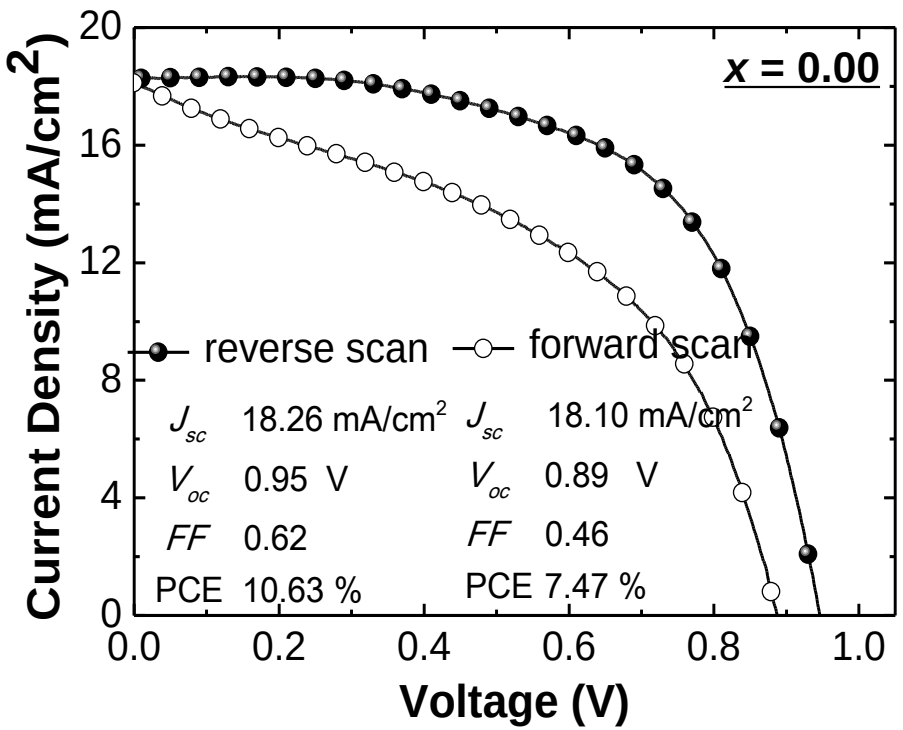


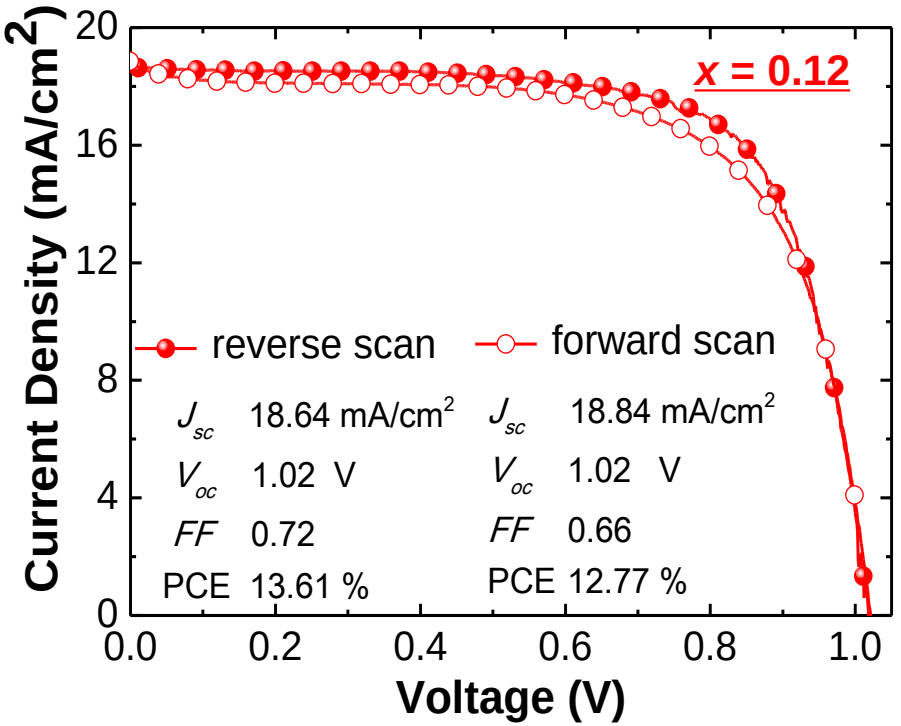
(Samples from: SKKU Univ.)

- **Characterization of electrical properties as a function of Br concentration**

- Conductive atomic force microscopy : contact mode (Pt/Ir coated Si tip)
- Kelvin probe force microscopy : non-contact mode (Pt/Ir coated Si tip)
- Piezoelectric force microscopy : contact mode (Co-coated Si tip)
- SEM, EDS

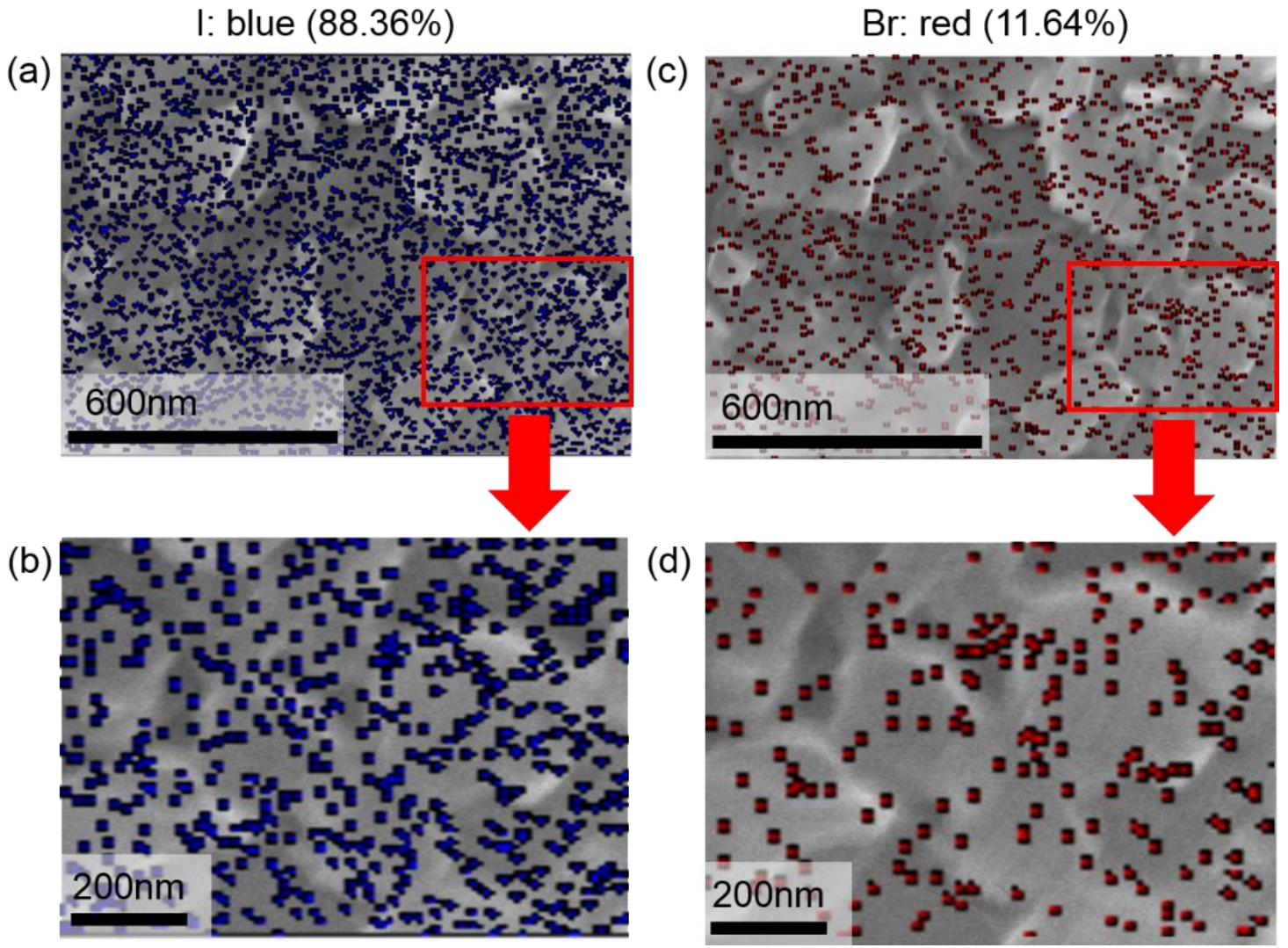
Efficiency of the perovskite solar cells with different Br





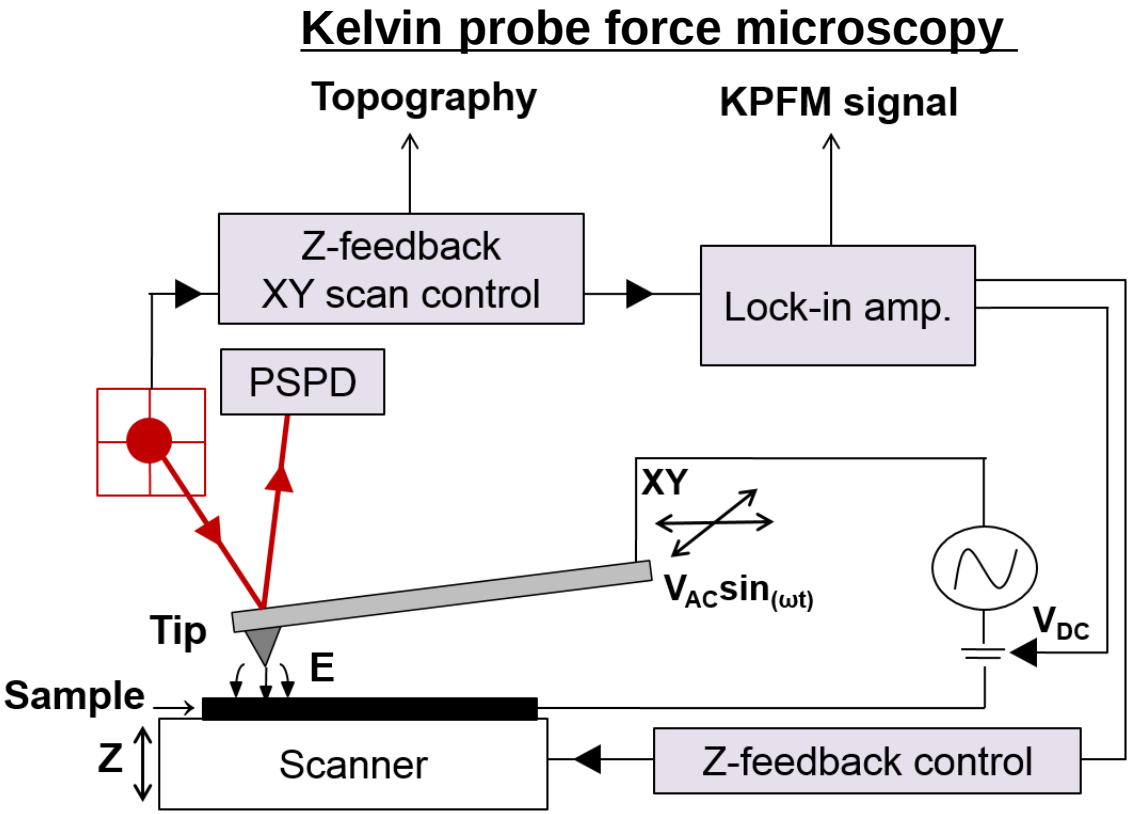
- Best performing perovskite solar cell (*x*=0.12) efficiency of 13.6%, J_{SC} of 18.64 mA/cm^2, V_{OC} of 1.02 V, FF of 0.72.
- A strong hysteric behavior in the J-V curve of x=0.00 perovskite solar cell

Composition distribution of I and Br in perovskite layer



Kelvin probe force microscopy

- Observing potential difference near the grain boundaries
- Measuring work function of the sample surface
- Expecting electron-hole carrier transport



$$F(z) = -\frac{1}{2}\Delta V^2 \frac{dC(z)}{dz}$$

$$F = F_{DC} + F_{\omega} + F_{2\omega}$$

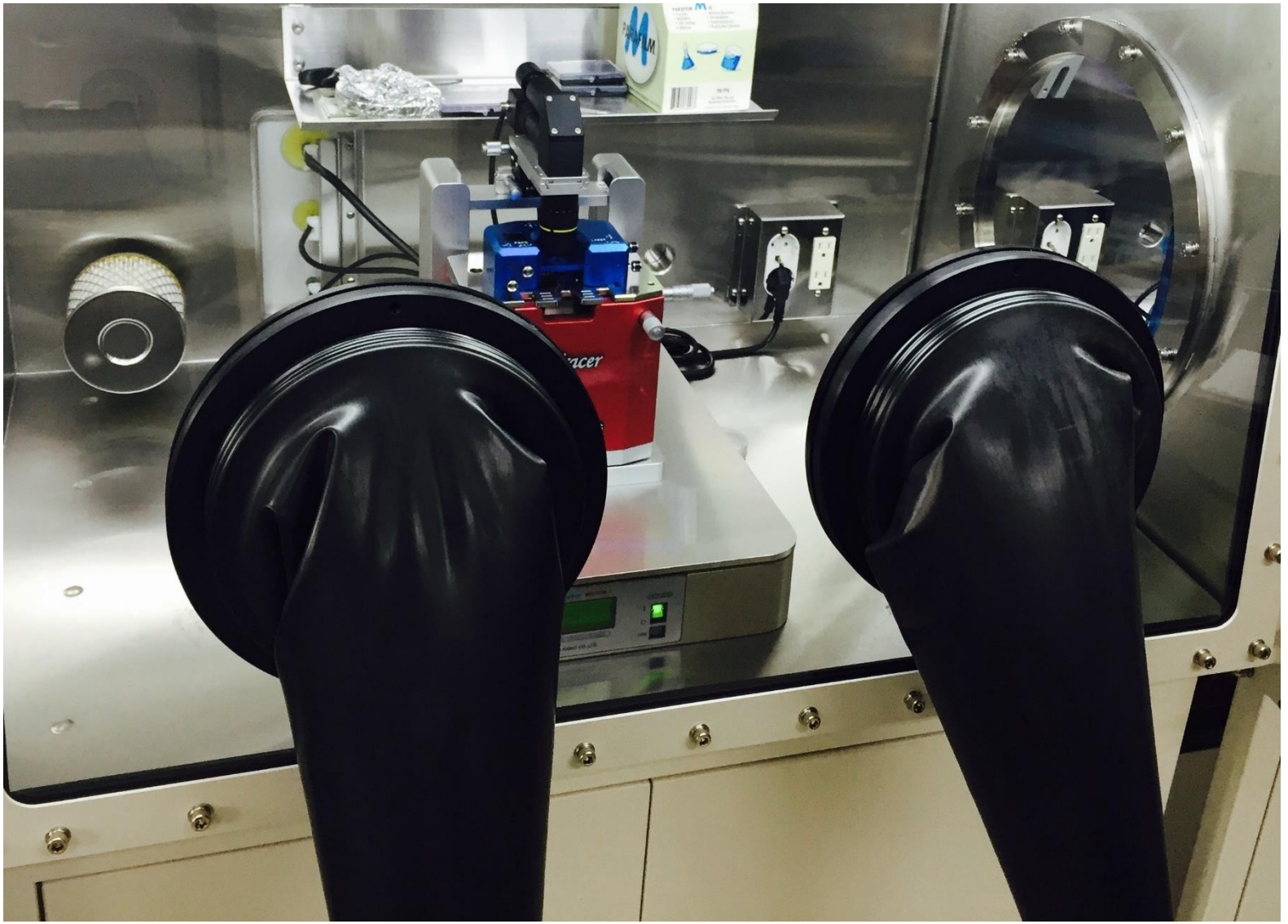
$$F_{DC} = \frac{dC}{dz}\left[\frac{1}{2}(V_{DC} \pm V_{CPD})^2\right]$$

$$F_{\omega} = -\frac{dC}{dz}(V_{DC} \pm V_{CPD})V_{AC}\sin(\omega t)$$

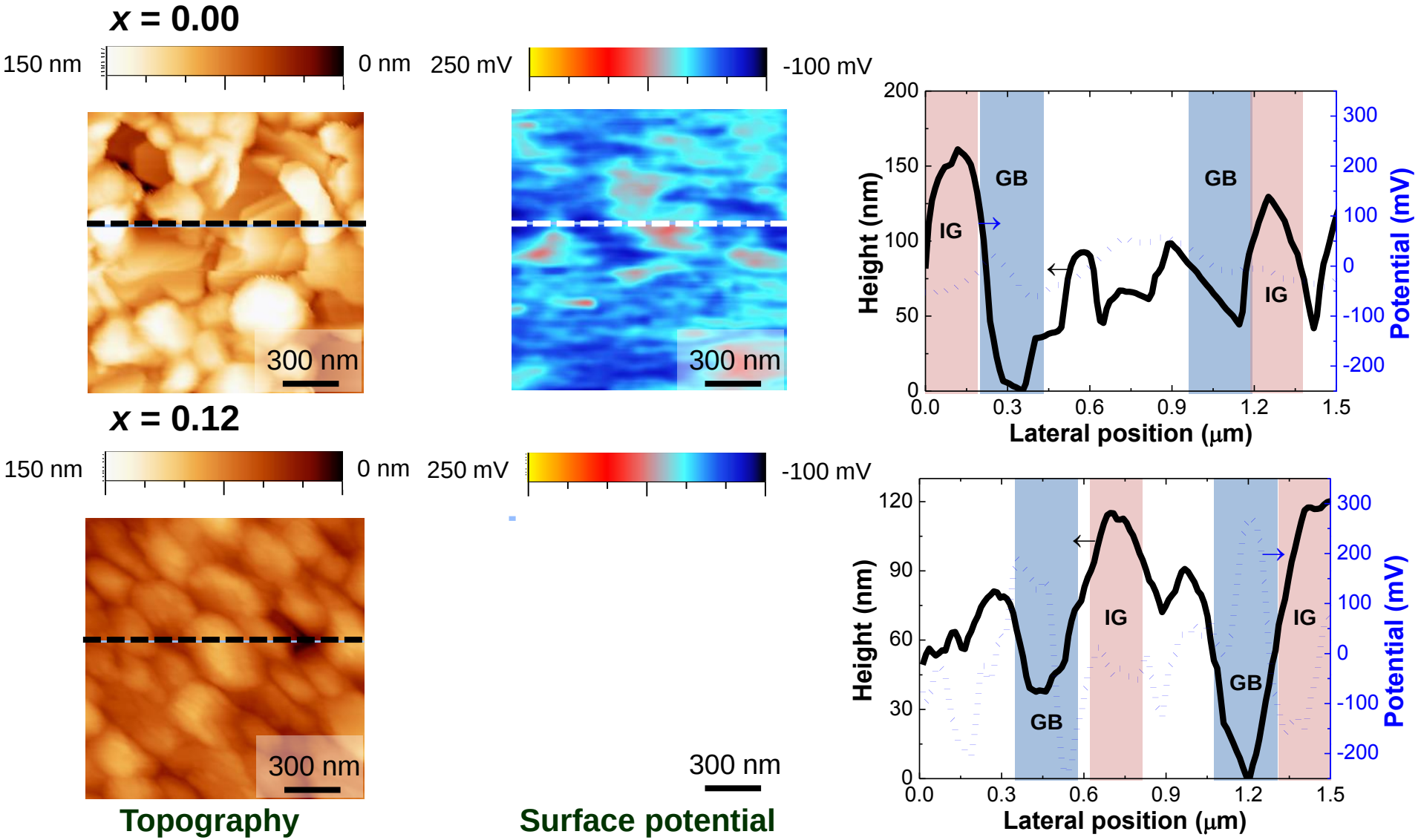
$$F_{2\omega} = \frac{1}{4}\frac{dC}{dz}V^2{}_{AC}\left[\cos(2\omega t) - 1\right]$$

G. Y. Kim *et al*. Nano Convergence 1 (2014) 27

A new glove box AFM system under controlled ambient

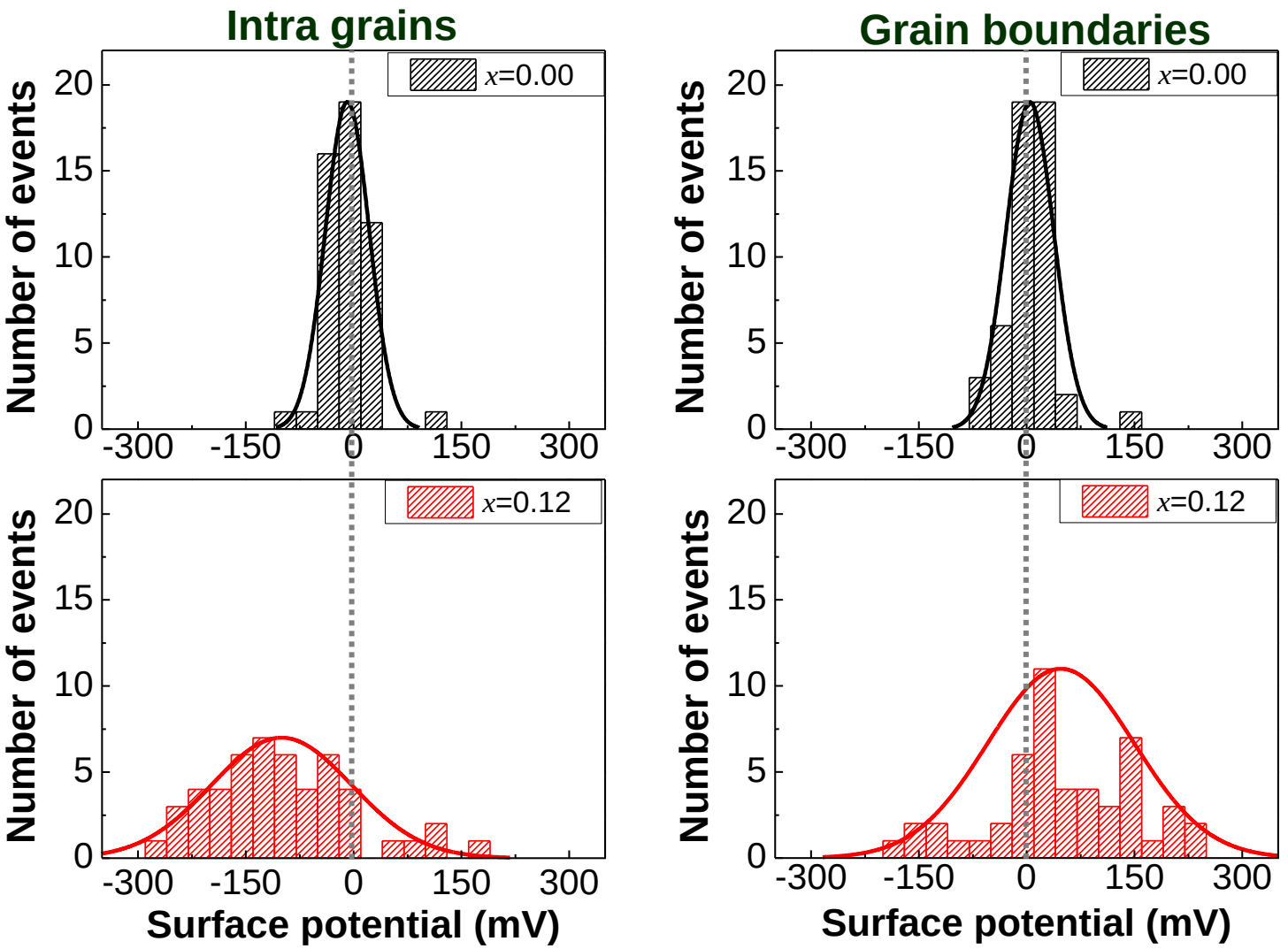


Surface potential mapping of perovskite surfaces



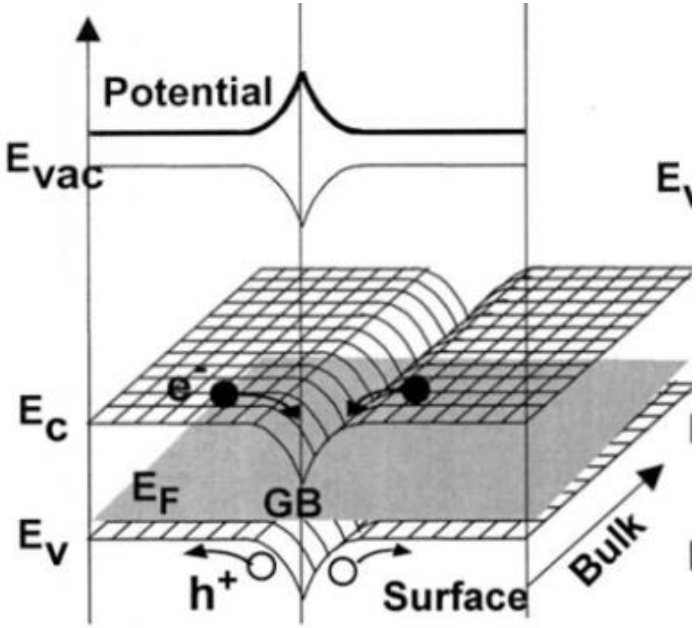
- Br containing perovskite film shows high potential different near the GBs.

Potential distribution of perovskite at IGs and GBs



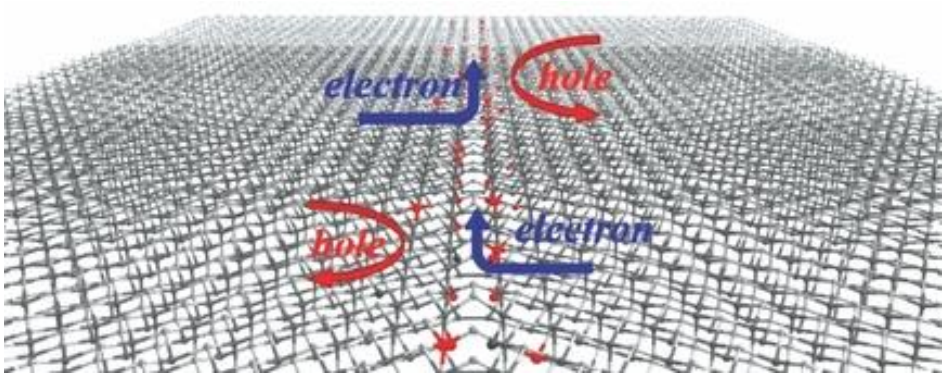
Various GB models of CIGS and CZTSe

GB model in CIGS



Jiang *et al*., Appl. Phys. Lett., **84** (2004) 3477

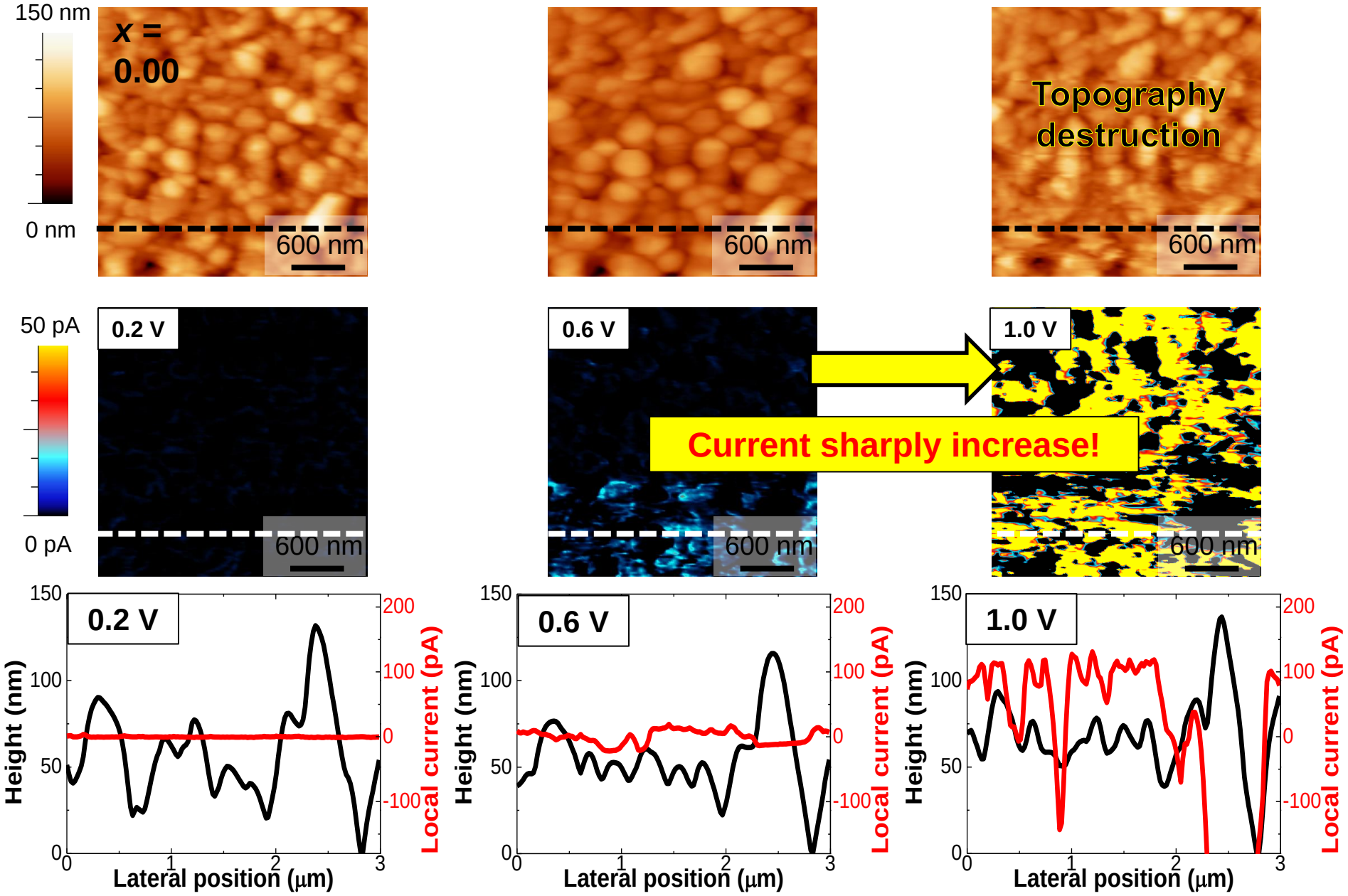
GB model in CZTSe



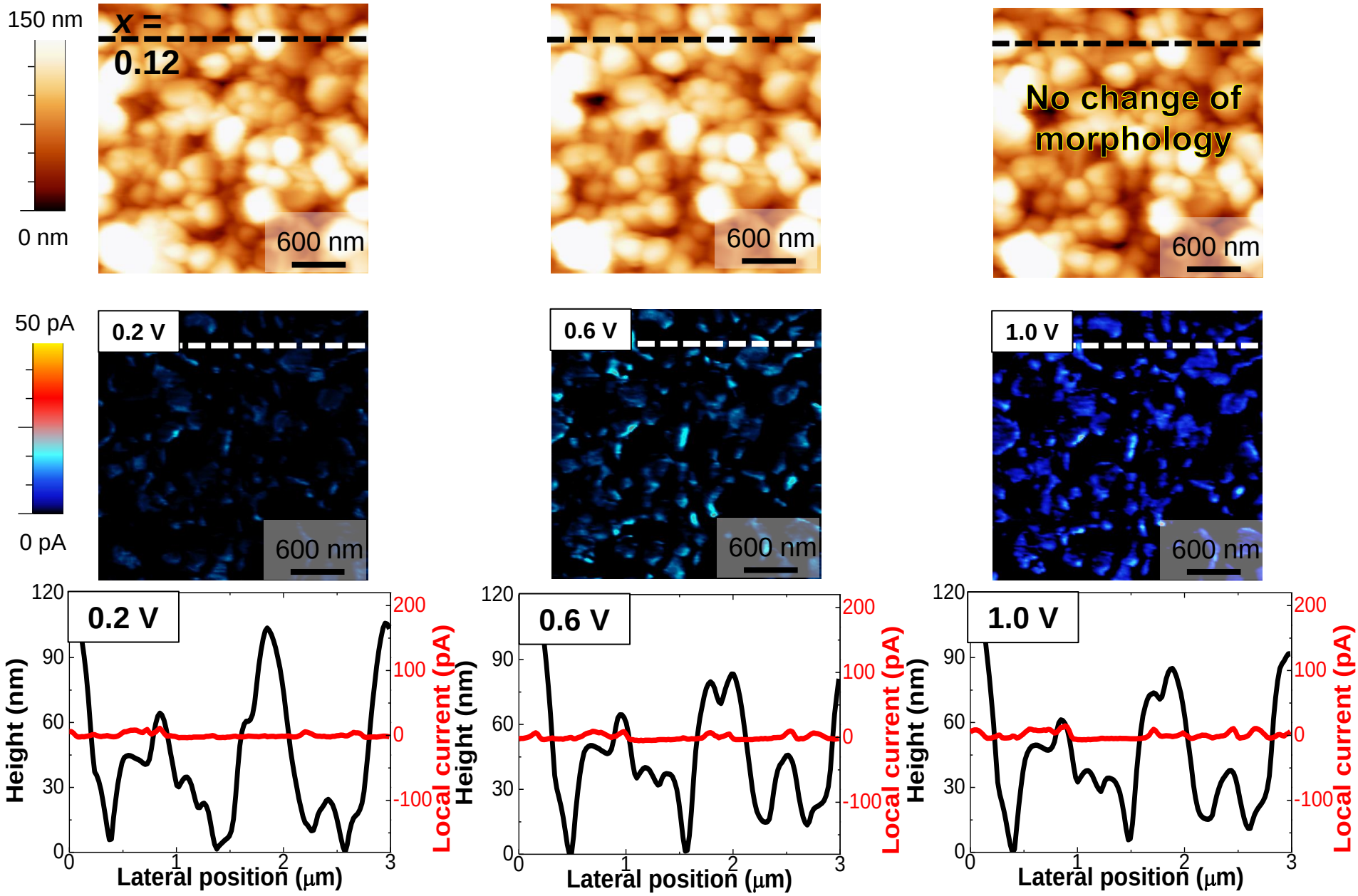
W.-J. Yin *et al*. Adv. Energy. Mater. **4** (2014)

- Local built-in potential inducing a downward energy band bending, which suppress the recombination in CIGS
- Downward band bending near GBs in CIGS and CZTSe forming hole barrier inside of the GBs and helping carrier separation

Local current mapping of the perovskite surfaces

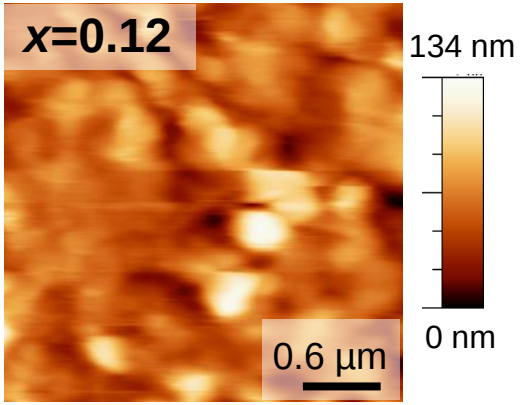


Local current mapping of the perovskite surfaces

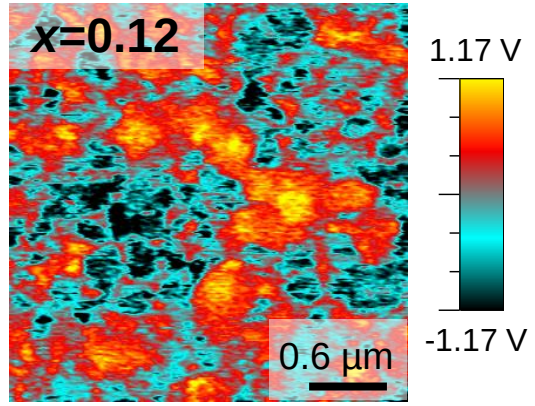


$CH_3NH_3Pb(I_{1-x}Br_x)_3$ Ionic bound charge? Ferroelectricity?

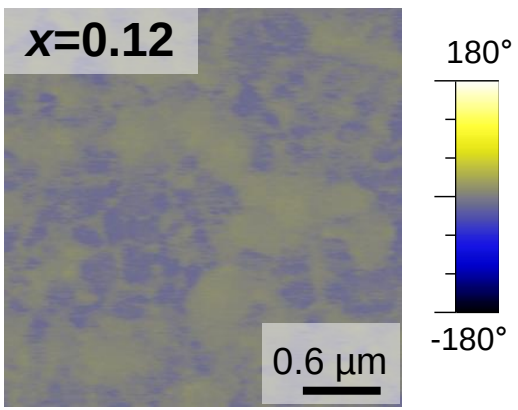
Topography



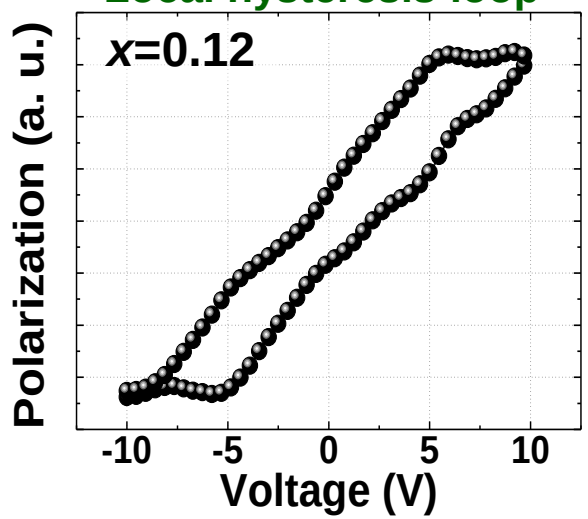
Amplitude



Phase



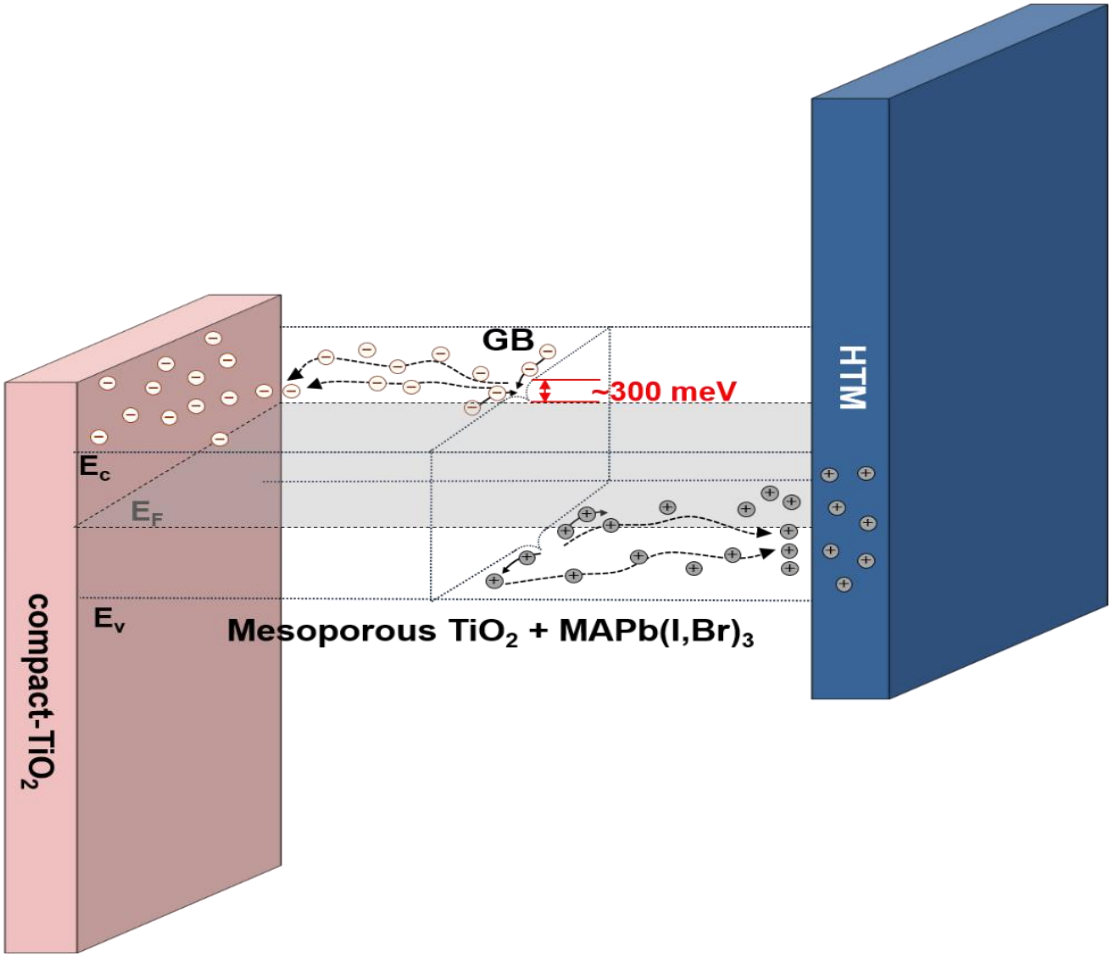
Local hysteresis loop



G. Y. Kim *et al*. J. Phys. Chem. Lett. **6** (2015) 2355-2362

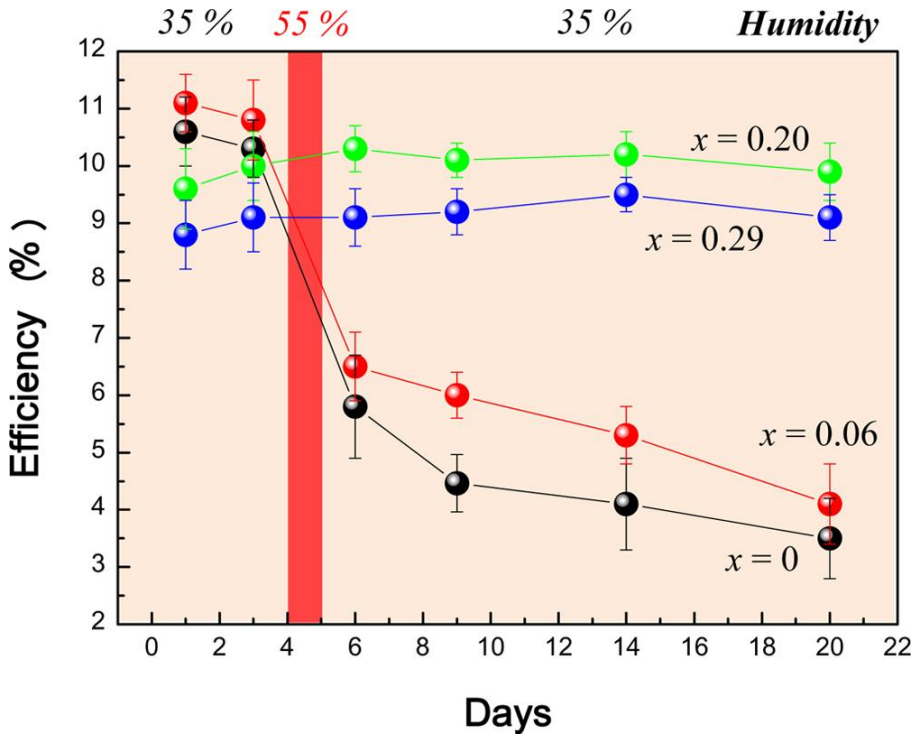
- Different amplitudes and phase signals can be observed at the spatial grain and GBs.
- Phase signal of the <u>x = 0.12 sample shows a small difference and a local well-saturated hysteretic loop in the grains</u>.

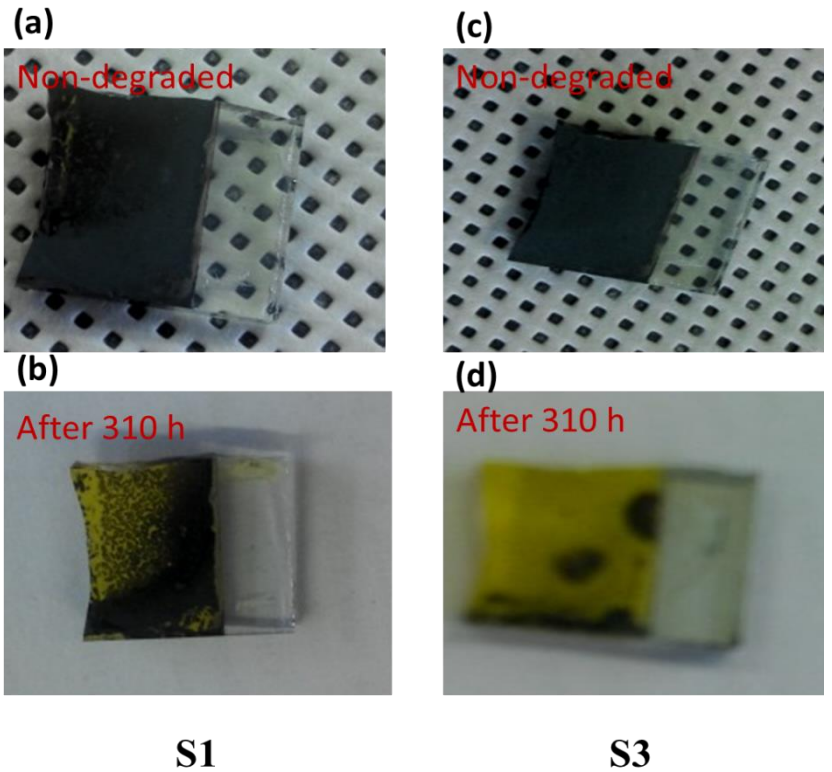
Electron-hole carrier transport near GBs in perovskites



- Separation of the electron−hole carrier from the perovskite layer to mesoporous TiO_2 layer
- Improvement the carrier separation due to the charged GBs (potential value at GBs ～300 mV, high local built-in potential)

Chemical and device instability of perovskite solar cells



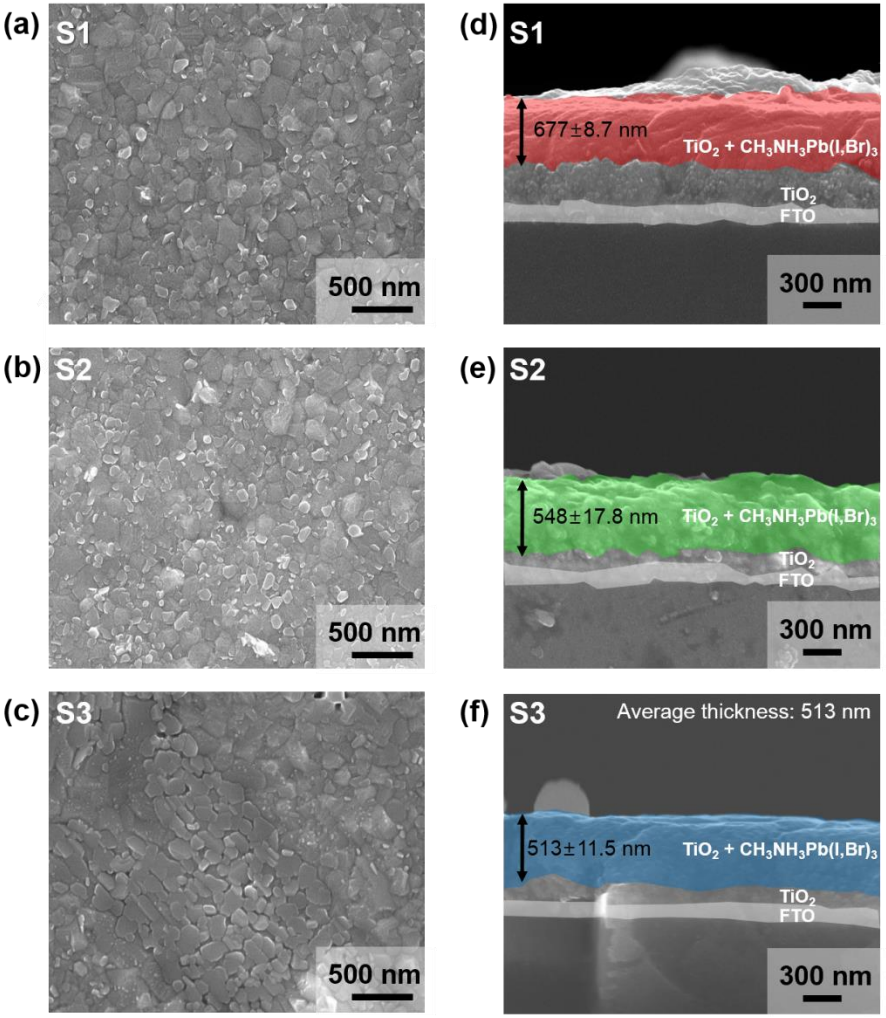


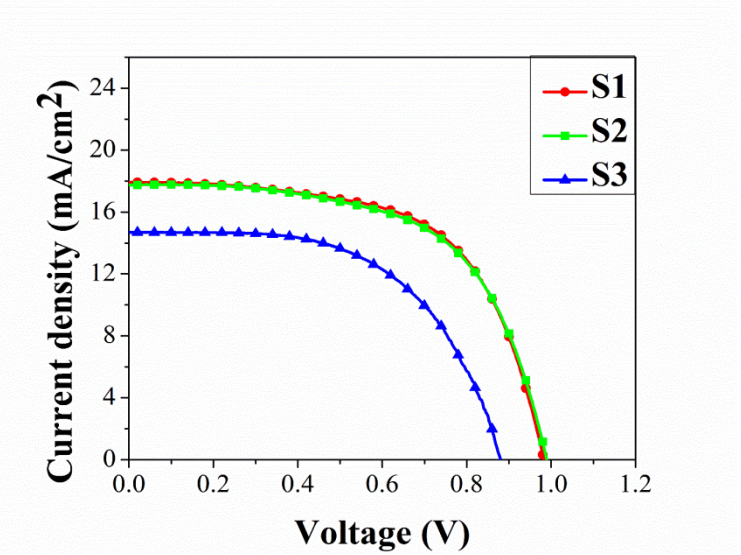
Power conversion efficiency variation of the heterojunction solar cells based on $MAPb(I_{1-x}Br_x)_3$ (x = 0, 0.06, 0.20, 0.29) with time stored in air at room temperature without encapsulation. The humidity was maintained at 35%, and the cells were exposed to a humidity of 55% for one day on the fourth day to investigate performance variation at high humidity.

Noh and Seok *et al*. Nano. Lett. **13** (2013) 1764-1769

B. P. Nguyen and G. Y. Kim et al. (unpublished)

Description of the $CH_3NH_3Pb(I,Br)_3$ perovskite solar cells

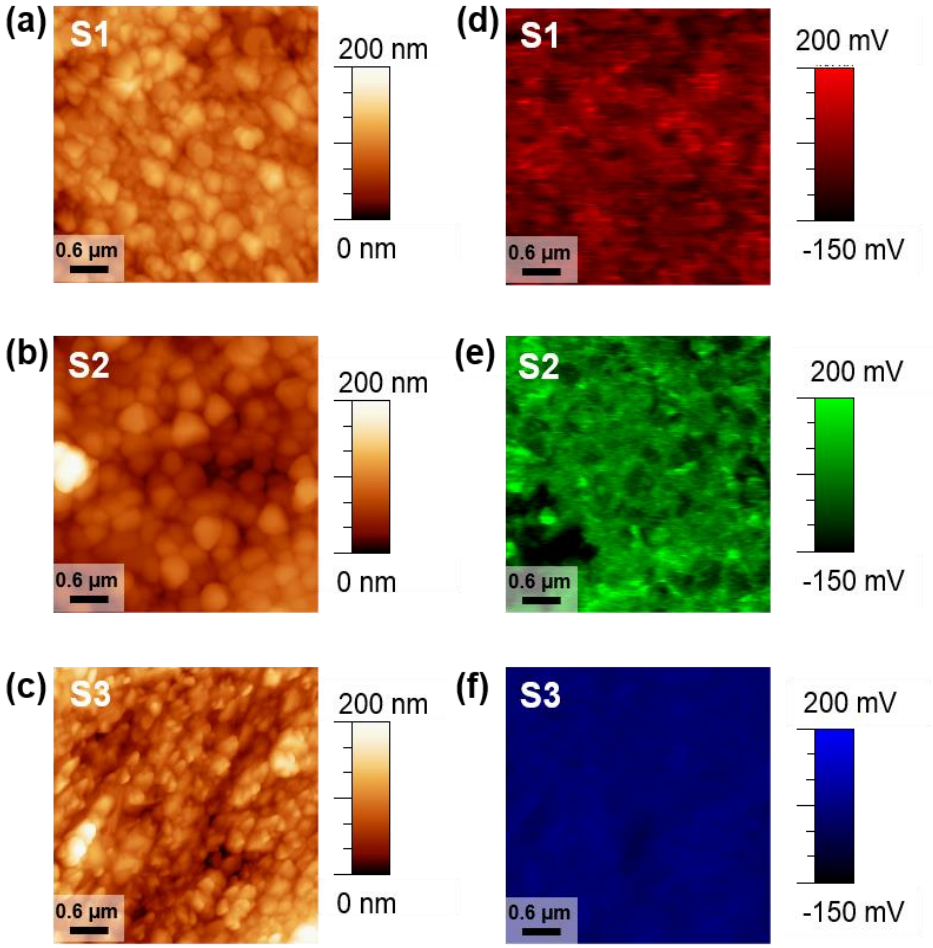




	J_{SC} (mA/cm²)	V_{OC} (V)	FF (%)	PCE (%)
S1	17.91	0.98	0.61	10.73
S2	17.75	0.989	0.60	10.58
S3	14.69	0.88	0.57	7.40

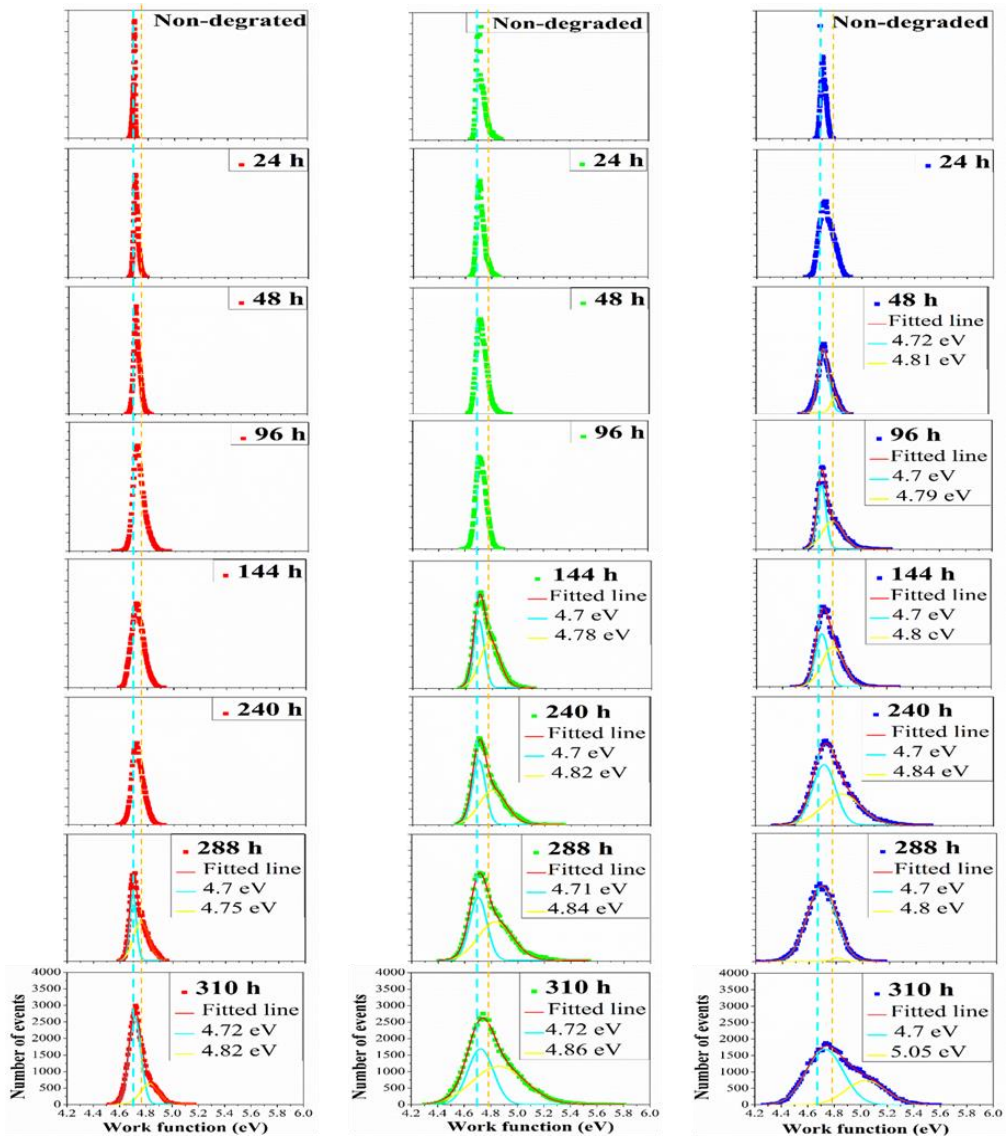
- We investigated the changes in the electrical properties of the $CH_3NH_3Pb(I_{1-x}Br_x)_3$ (x=0.13) perovskite materials with various thickness under atmospheric conditions

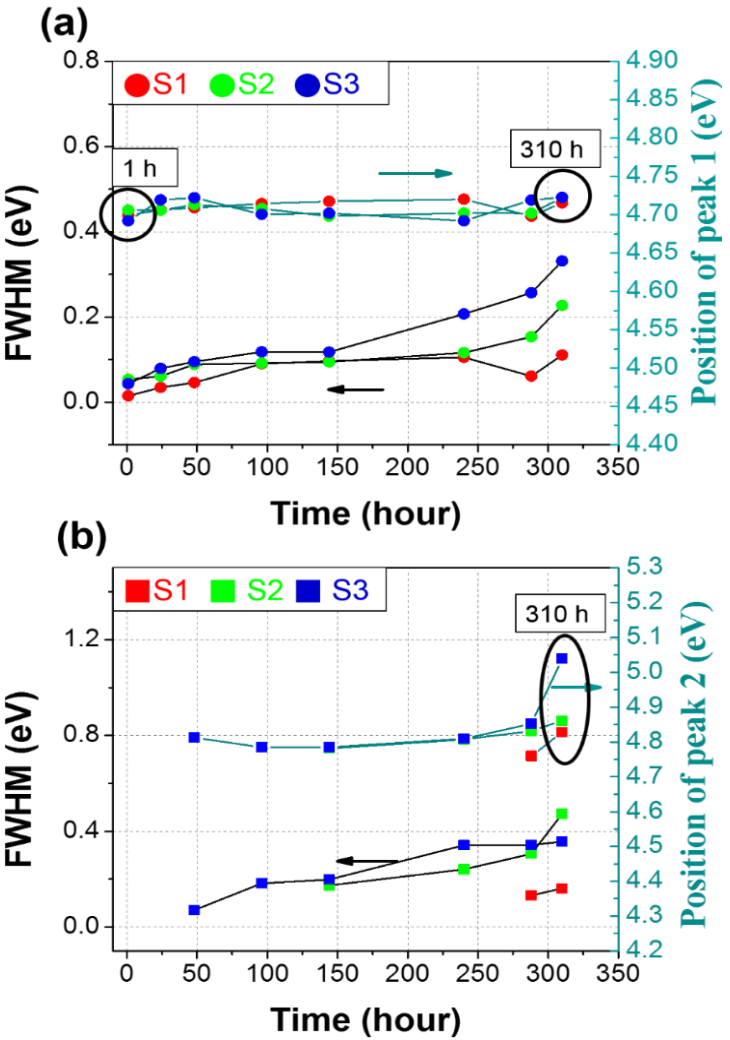
Change of the work function of $CH_3NH_3Pb(I,Br)_3$ (time dep.)



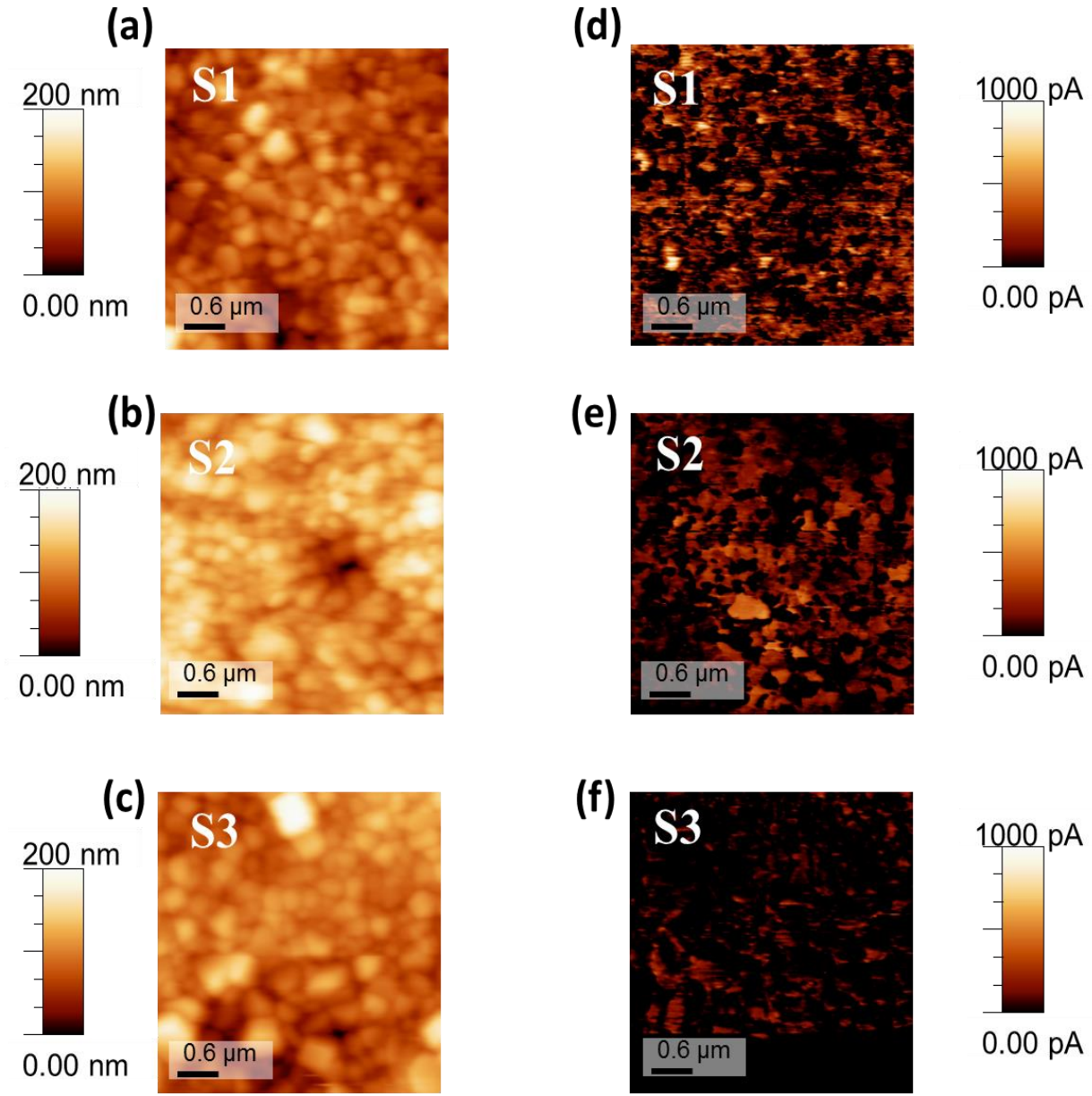
- (a) FWHM and peak shift of potential peak at 4.7 eV, which might be the major peak of perovskite.
- (b) FWHM and peak shift of potential peak at 4.8 eV, which is gradually move to higher energy and related to the degradation.

Work function distribution of perovskite

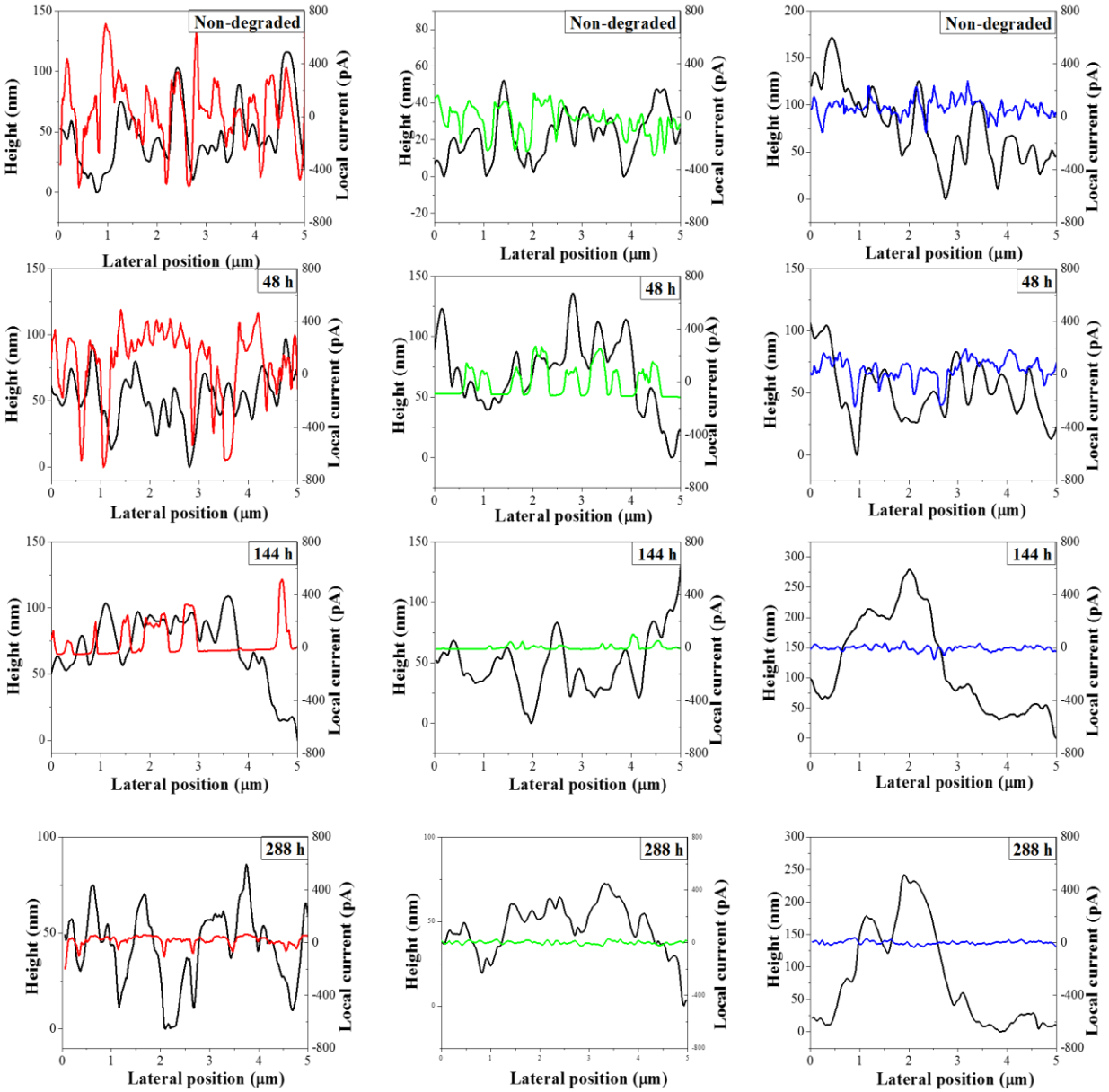




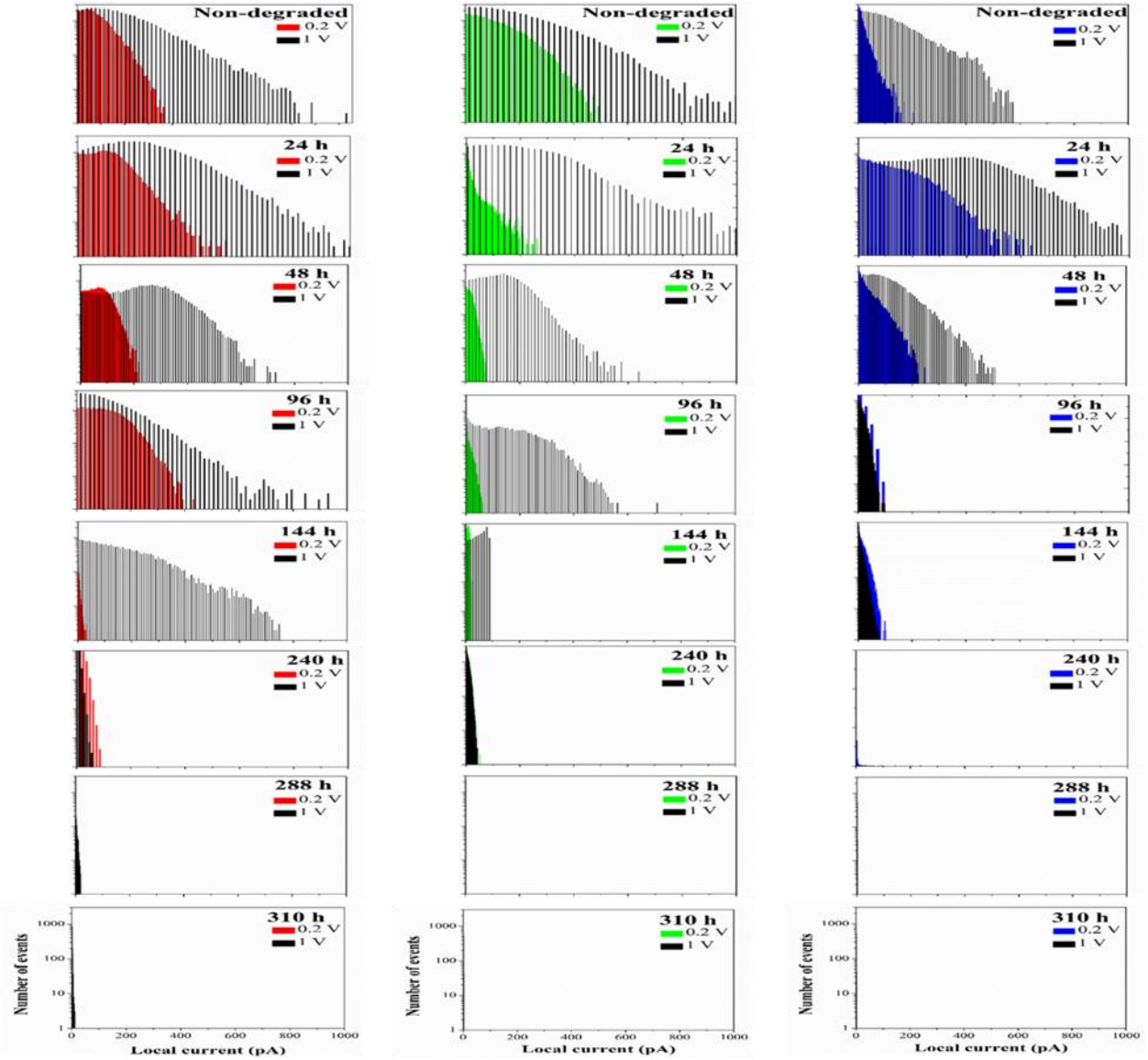
Current mapping of perovskite



Current profile of perovskite at IGs and GBs

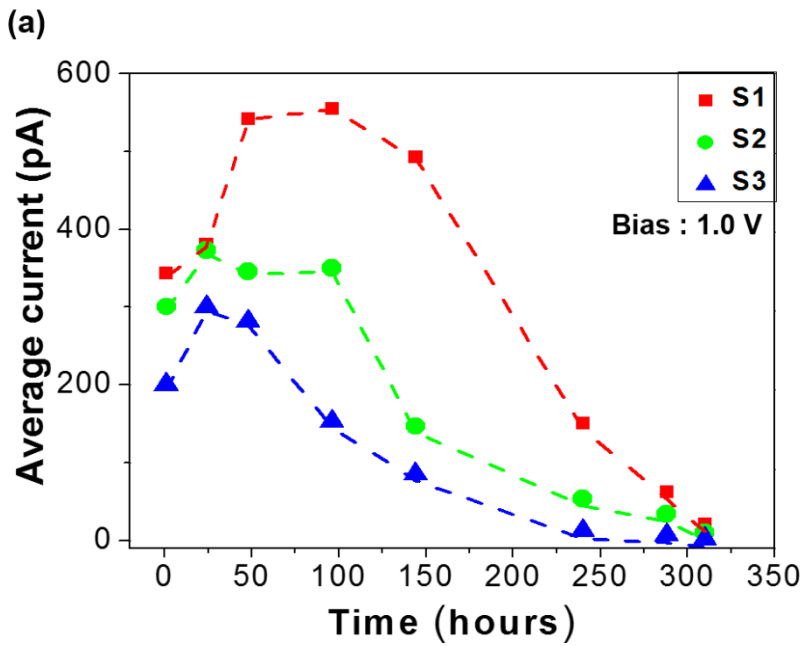


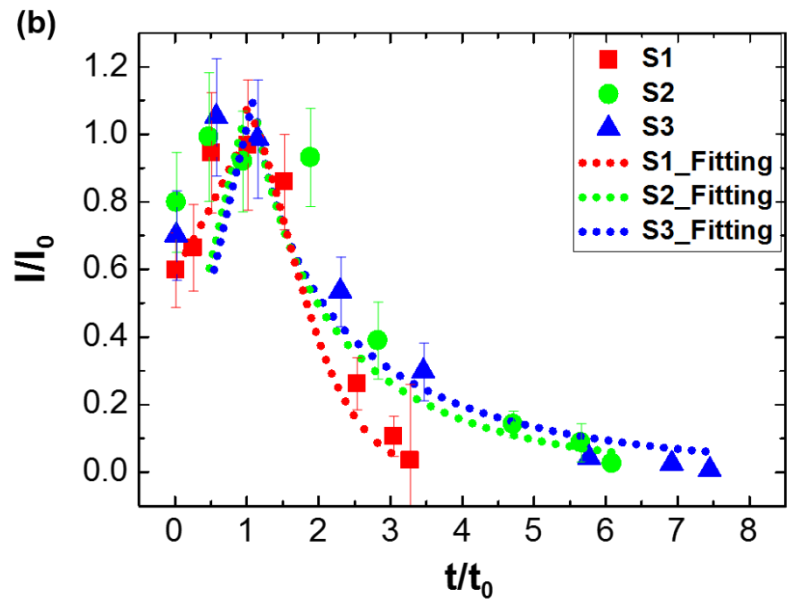
Current distribution of perovskite



S1 S2 S3

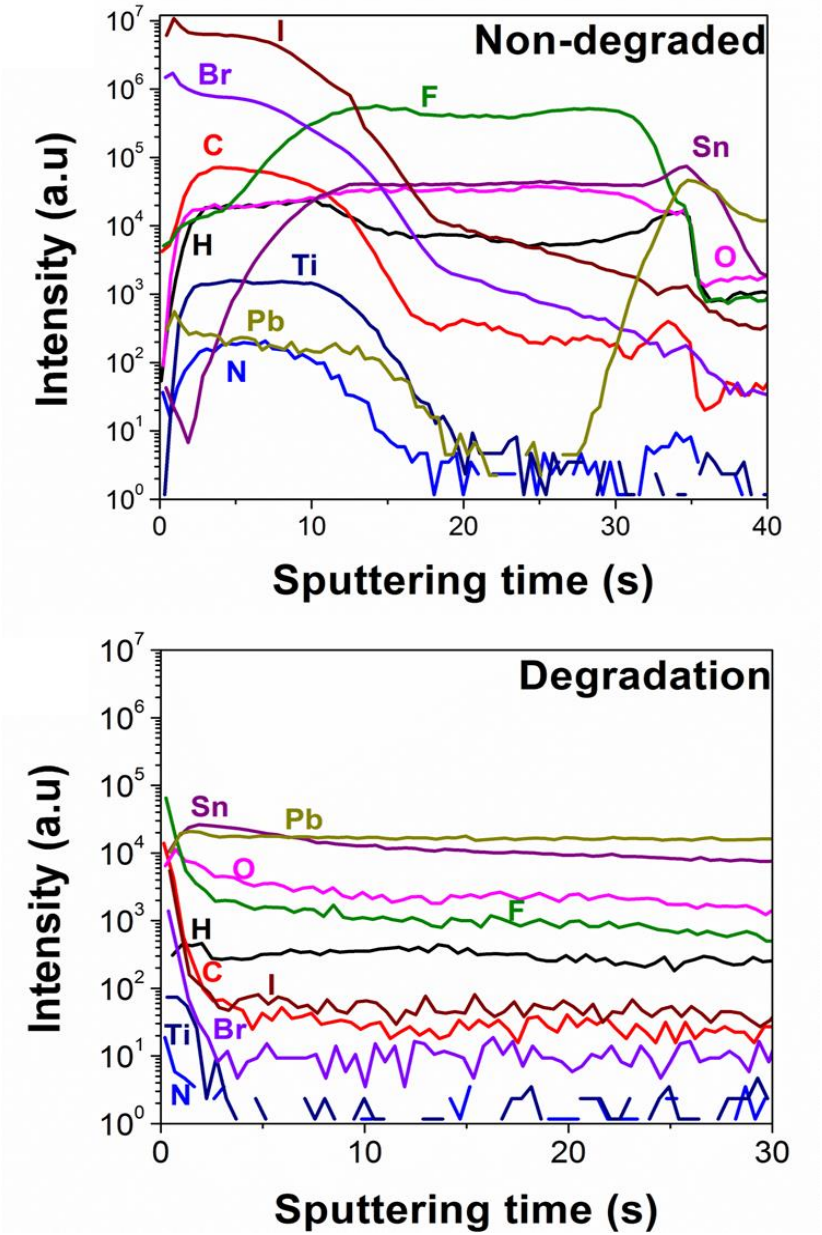
Change of the local current of $CH_3NH_3Pb(I,Br)_3$ (time dep.)

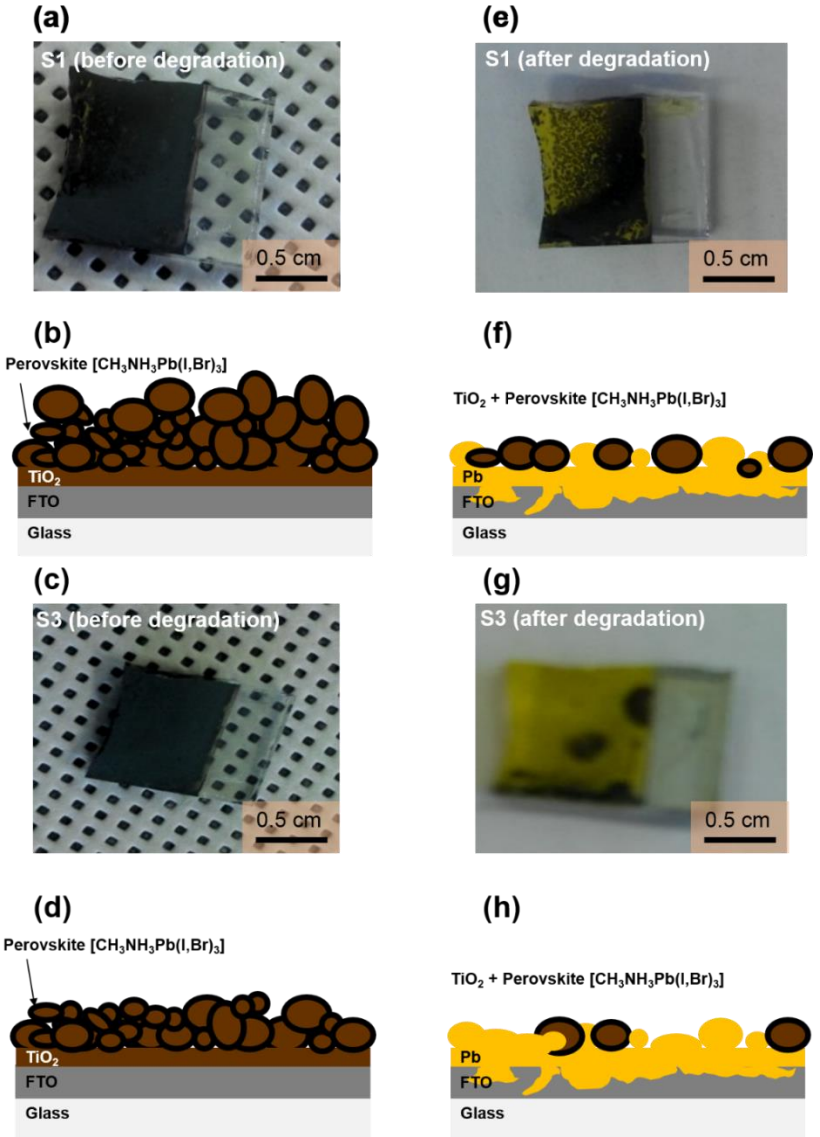




- Average local current value plotted from the current mapping at bias voltage 1 V of three perovskite samples with different thickness in ambient environment for 310 h storage.
- The local current flow of three samples increased in the first few days of storage in ambient conditions and decreased quickly after.

Composition profile and phase distribution of $CH_3NH_3Pb(I,Br)_3$





Summary

- A high, positively charged region appeared in the GBs and the local current (< 50 pA) flows through most of the grains in the x = 0.12 of perovskite thin films.
- Polarization properties of the Br-containing perovskite film shows a higher spot size in the domains relative to the grain size.
- Positively charged GBs to play a beneficial role in the perovskite thin-film solar cells by improving the electrical quality characteristics, such as the carrier collection and recombination.
- Thickest sample (~677 nm; meso-TiO_2+Perovskite layer) stored for 96 h, the contact potential exhibited little variation, and a gradual increase in the local current was also confirmed in the scanned current map.

- Dependence of grain size has been studied and will be submitted soon.
- Pb-free perovskites and Single crystals of I and Br are under study.