Scanning Probe Microscope: A powerful Tool for Imaging Nanoscale Charge Transport Properties

UNSW AUSTRALIA

Never Stand Still | Faculty of Engineering | School of Photovoltaic and Renewable Energy Engineering

Jae Sung Yun

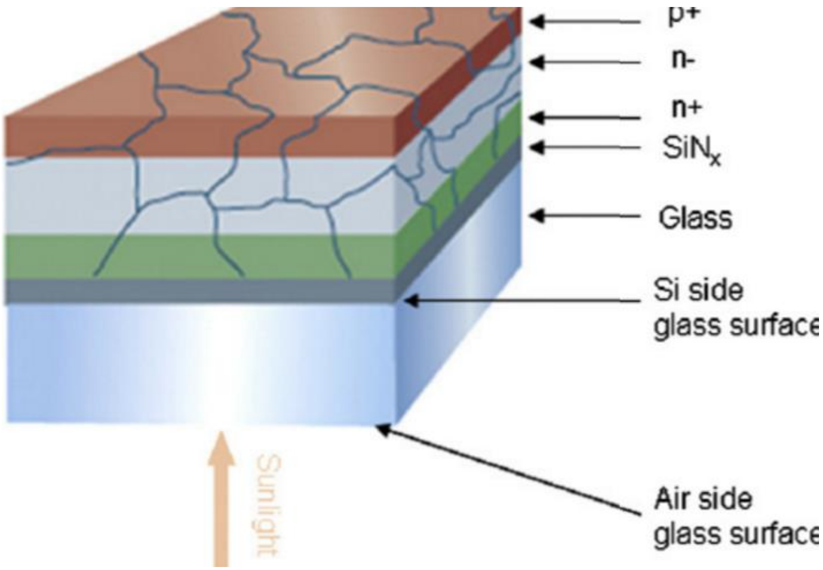
Australian Centre for Advanced Photovoltaics Fellow
UNSW, Australia

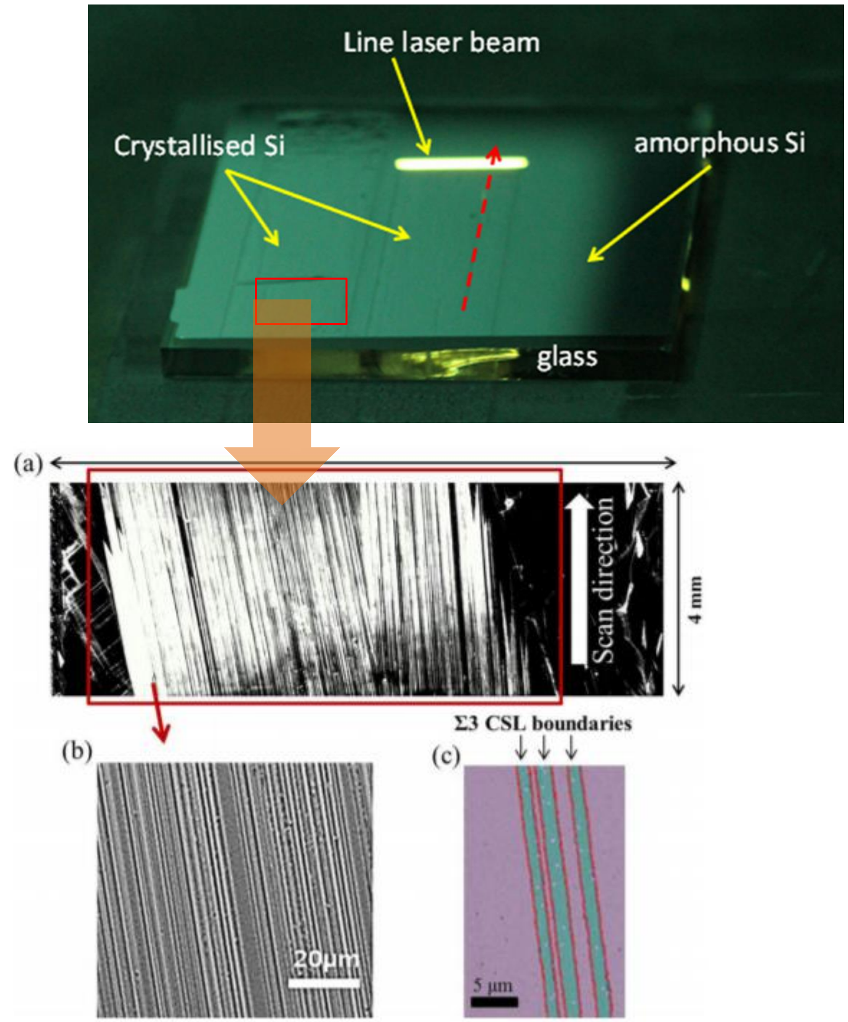
ACAP

CONTENTS

MOTIVATION

Crystalline Si thin film on Glass (CSG) Technology





J. Yun, et al. Appl. Phys. Lett. 2014

Any method to observe PV characteristics of structural defects in nanoscale?

"Spatial resolution of few tenth of nanometre is required"

ATOMIC FORCE MICROSCOPY

VOLUME 56, NUMBER 9 PHYSICAL REVIEW LETTERS 3 MARCH 1986

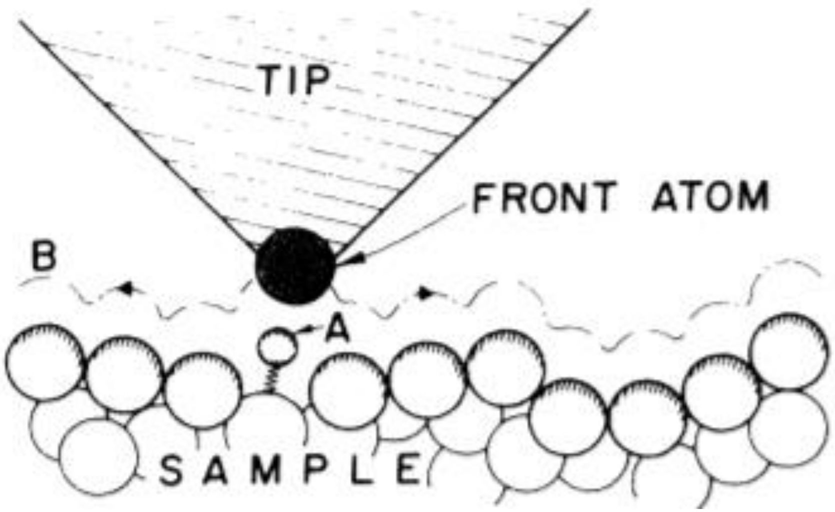
Atomic Force Microscope

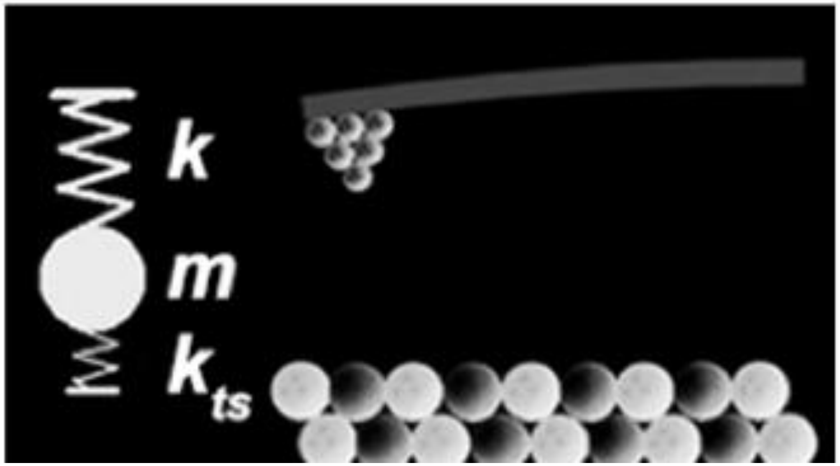
G. Binnig[a] and C. F. Quate[b]
Edward L. Ginzton Laboratory, Stanford University, Stanford, California 94305

and

Ch. Gerber[c]
IBM San Jose Research Laboratory, San Jose, California 95193

(Received 5 December 1985)

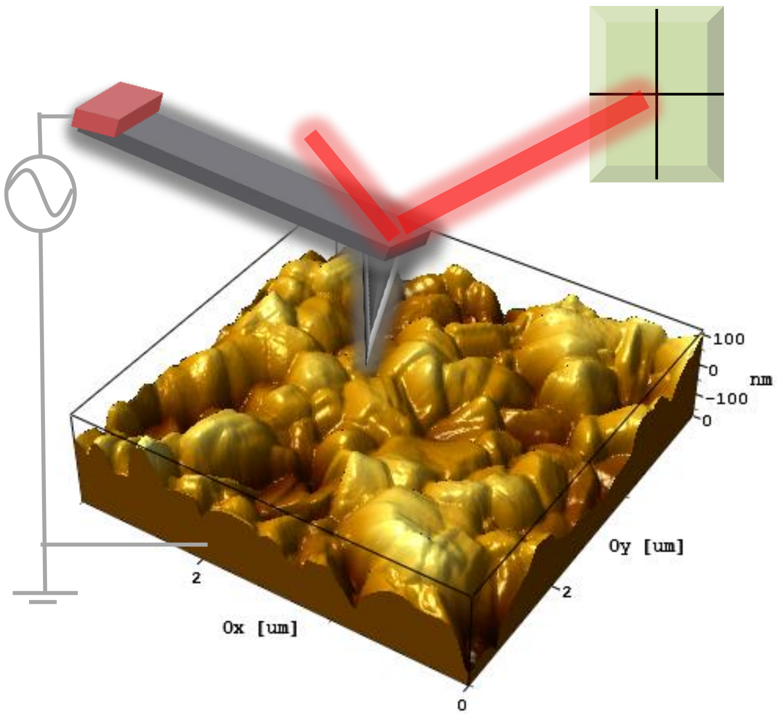


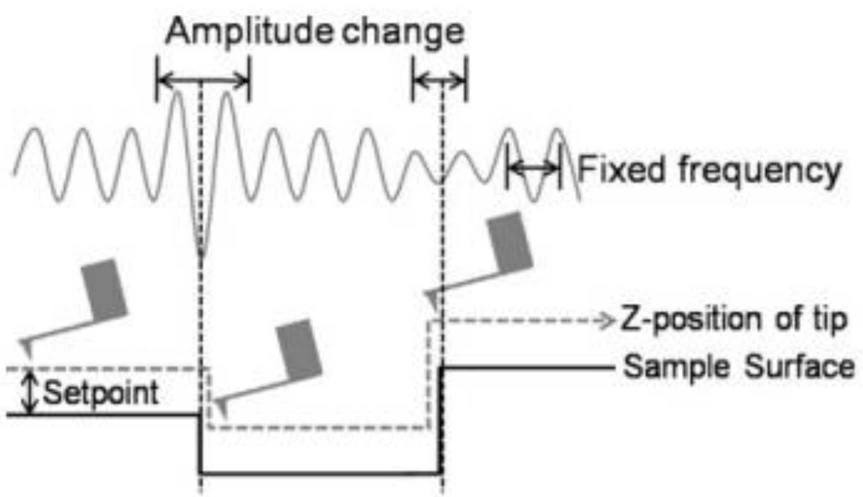


F. Giessibl, *Rev. Mod. Phys.* **75**, 949 (2003)

“Atomic interaction between tip and the sample”

NON-CONTACT MODE AFM

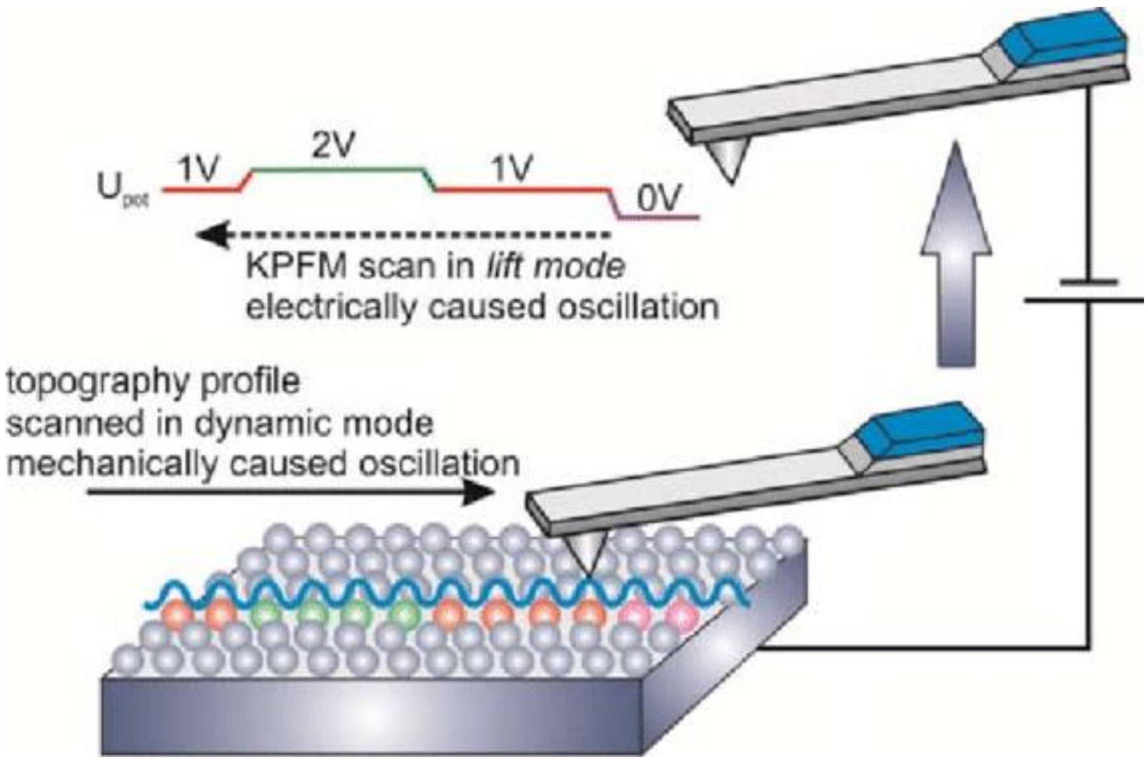




1. **Vibration at slightly above the resonance frequency of probe.**
2. **Rise to shift of the resonance frequency due to the interaction.**
3. **The changes in the oscillation amplitude are monitored and the feedback signals keeps constant the force gradient.**

Surface Science Reports 66 (2011) 1–27

KELVIN PROBE FORCE MICROSCOPY

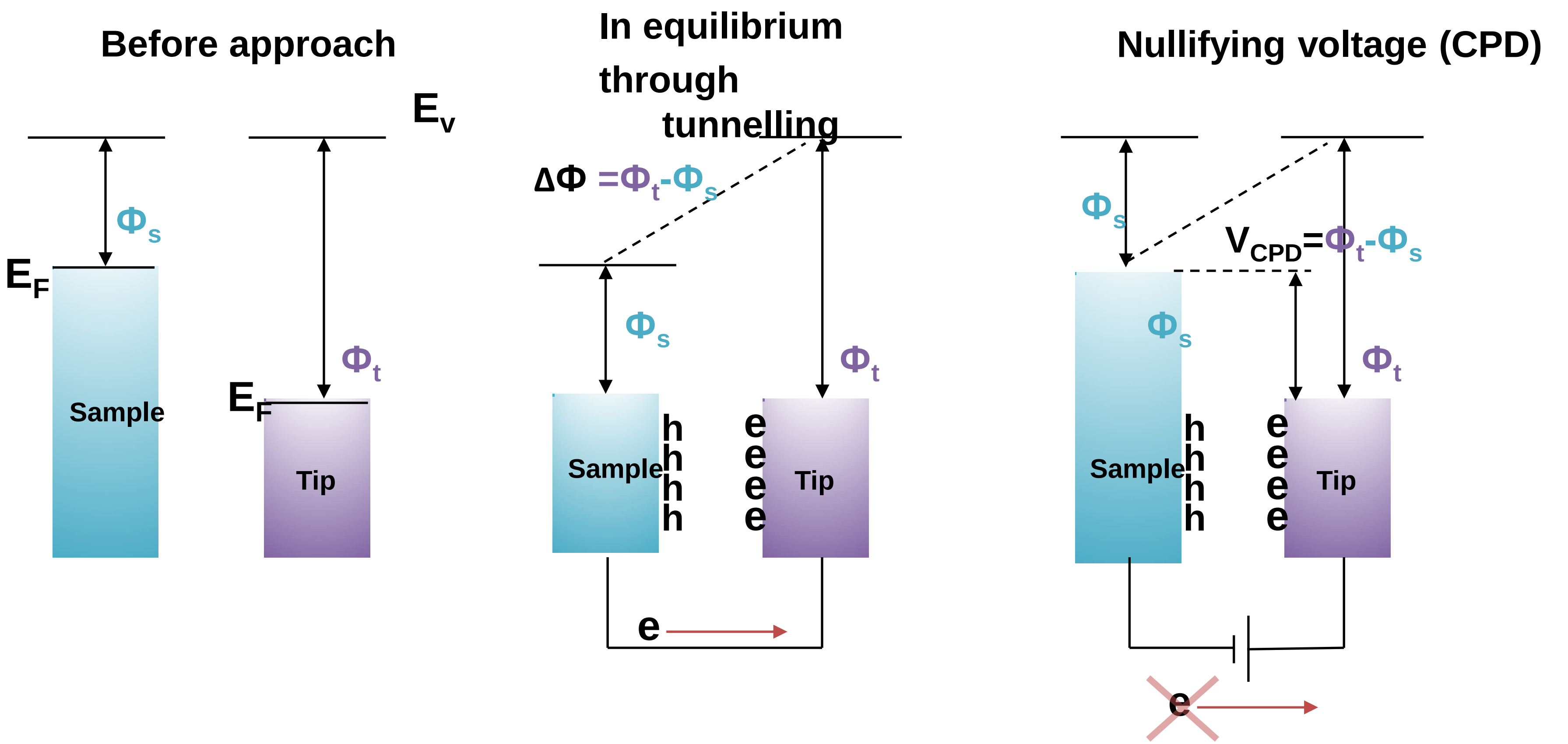


Przegląd Elektrotechniczny 91.9 (2015): 166-169.

1st pass → Height
2nd pass → CPD

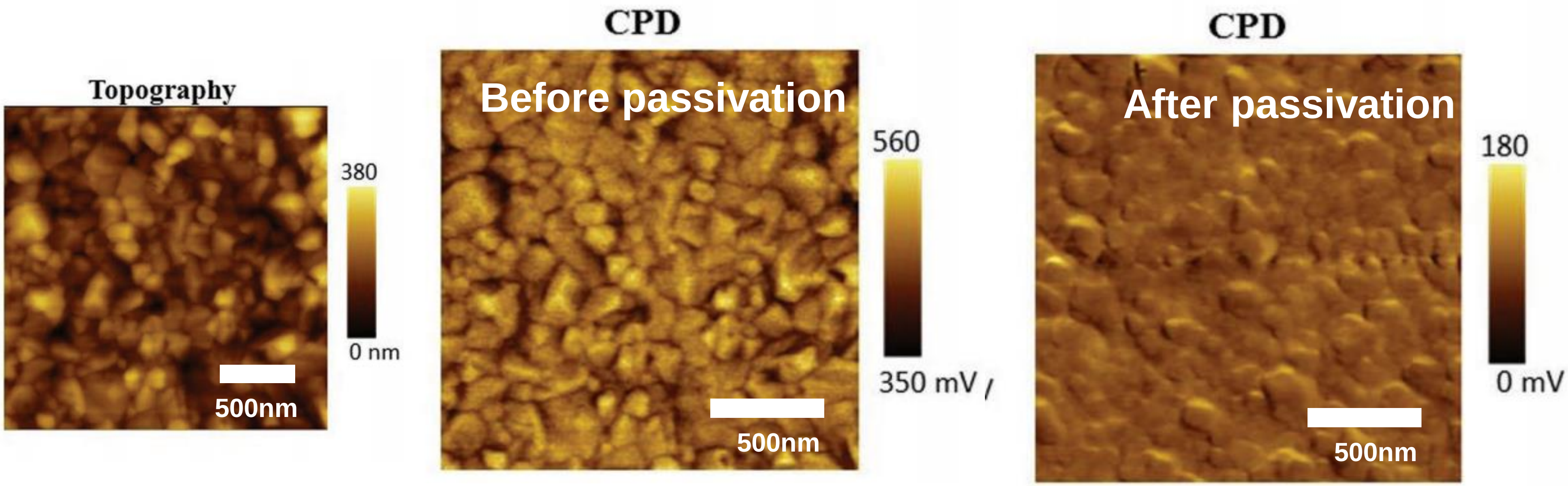
Imaging height signal and CPD signal at the same spot!

CONTACT POTENTIAL DIFFERENCE (CPD)



An **electrostatic force** exists between tip and sample due to work function difference and **DC voltage** is applied to **nullify** the force. >**<u>1 nm and >1 mV spatial resolution</u>**

CPD measures work function of a sample surface

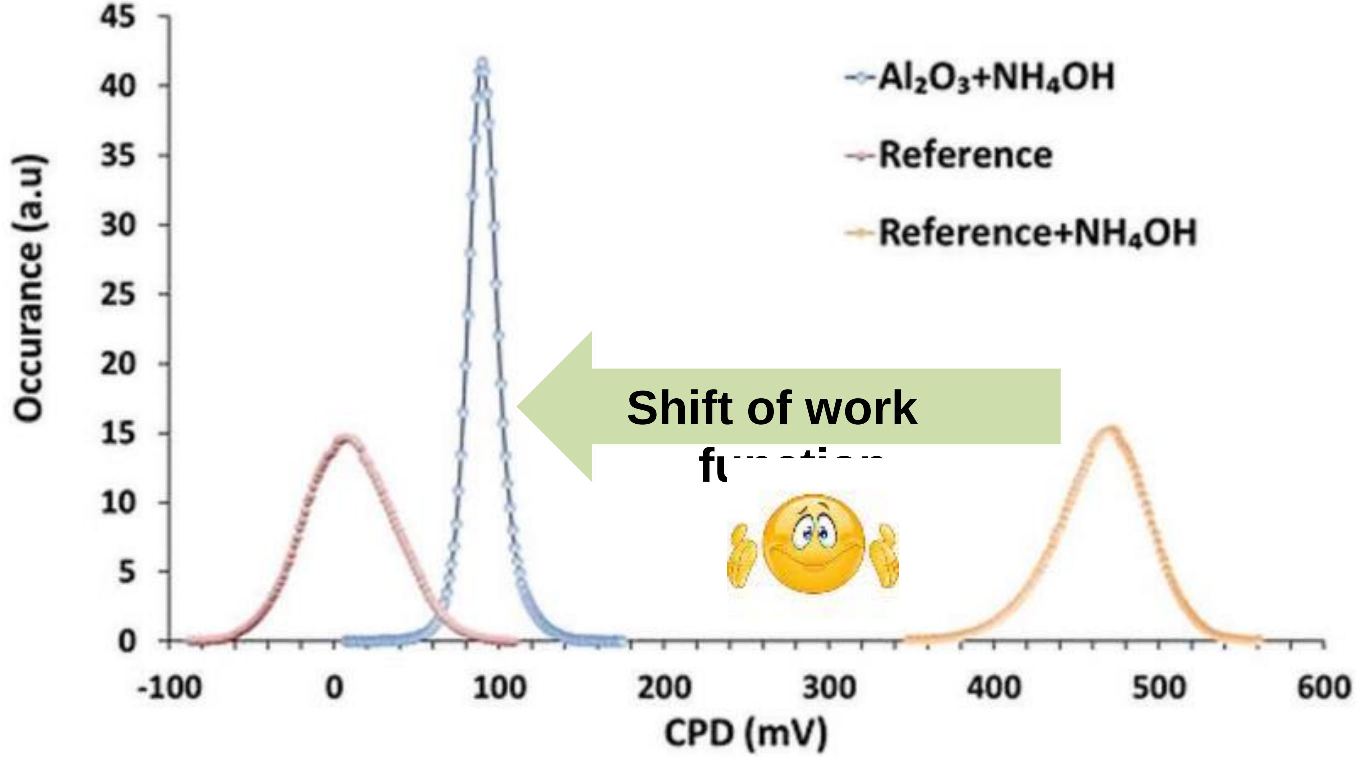


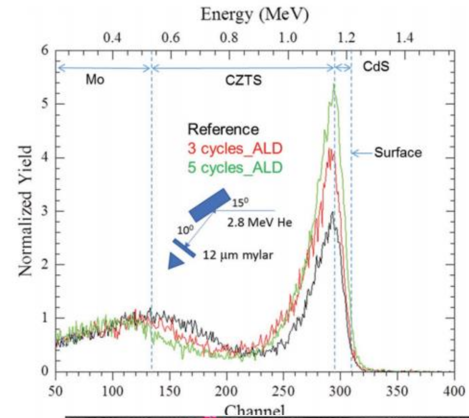
What does this mean to us?

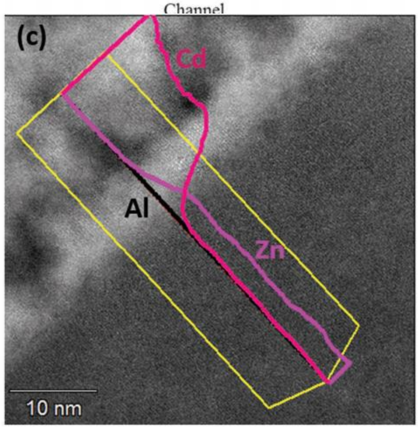
Advanced Energy Materials 8 (23), 1701940

CONTACT POTENTIAL DIFFERENCE (CPD)

Narrower distribution







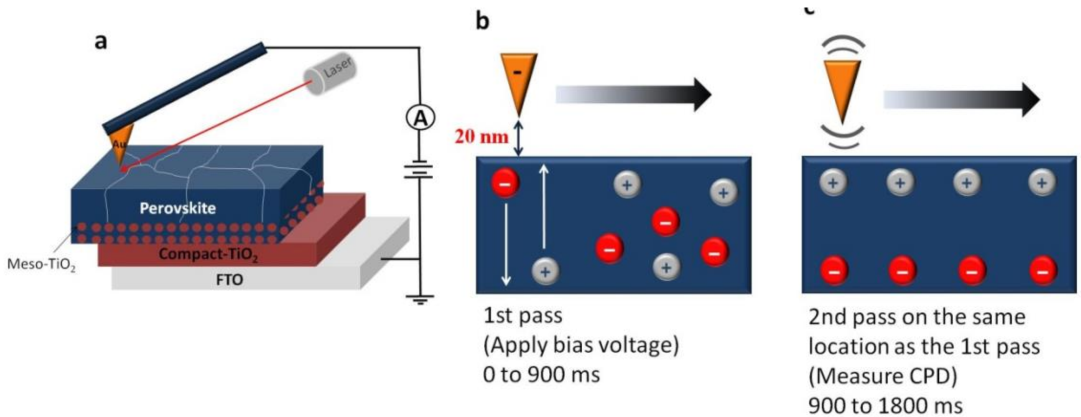
Advanced Energy Materials 8 (23), 1701940

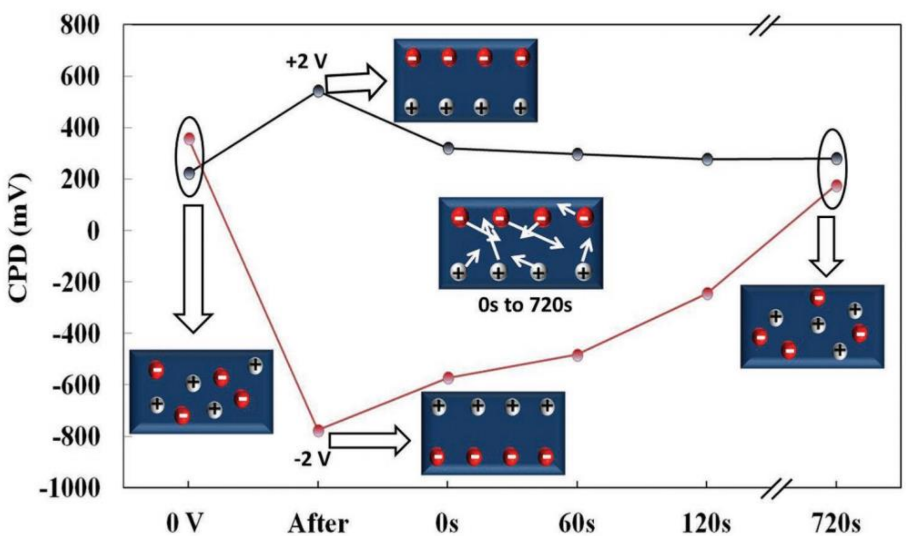
What made a shift of work function?

- **Charge carrier density, bandgap, surface states, surface dipole, crystal orientation**

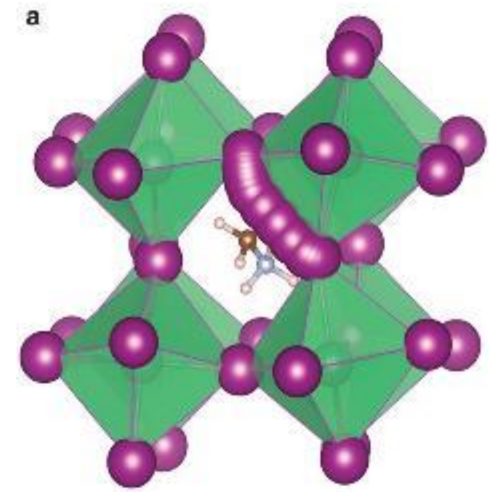
It is always good to have results from other techniques such as SIMS, TEM, XRD, etc.

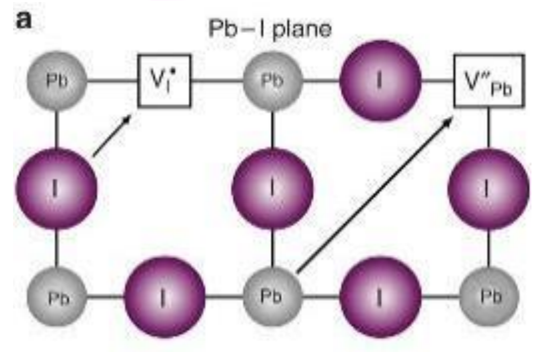
CONTACT POTENTIAL DIFFERENCE (CPD)





J. Yun et al. Advanced Energy Materials 6 (13), 1600330

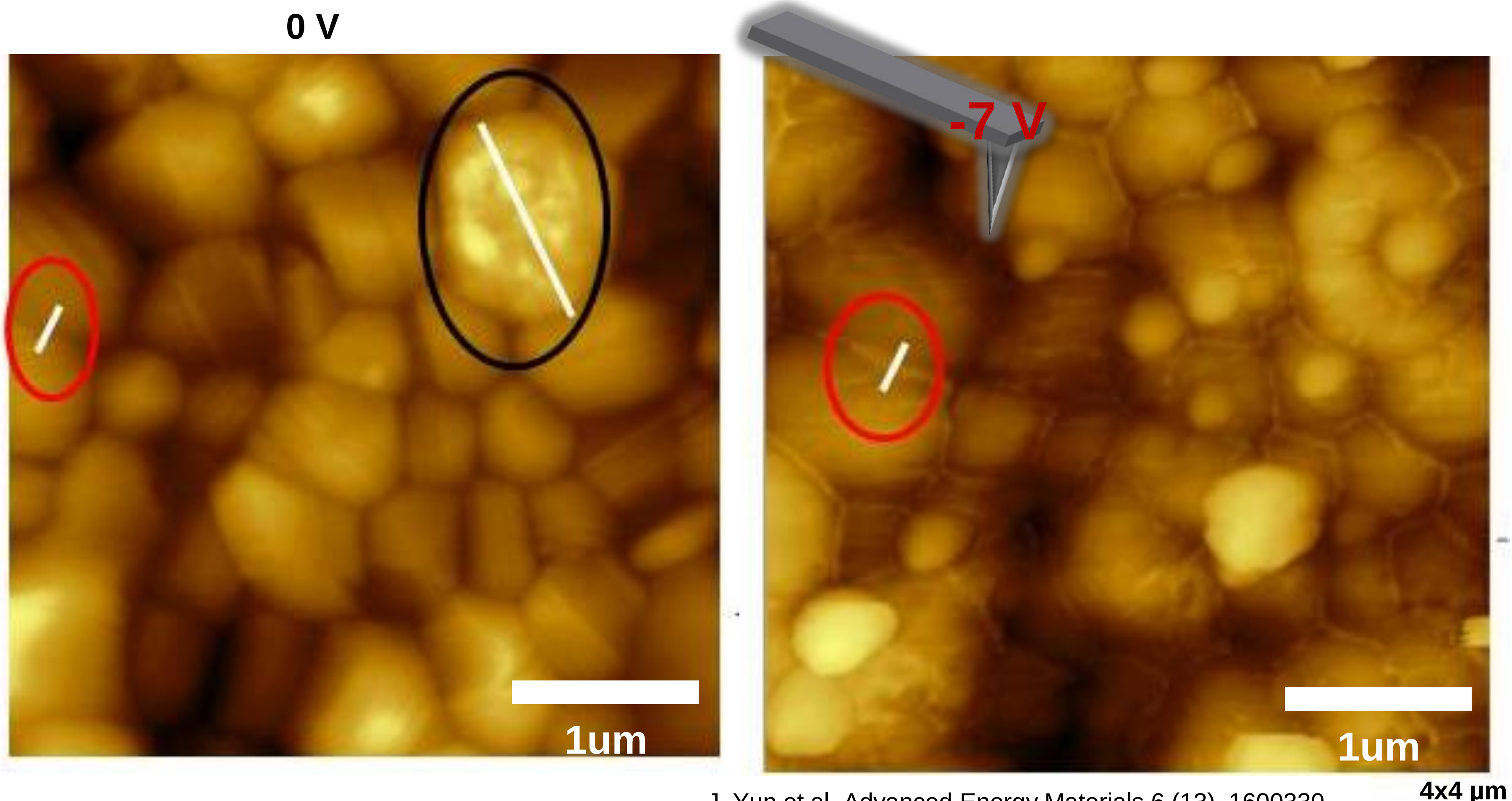




Nature Communications 6, 7497 (201

Iodide vacancies in halide perovskite changes work function

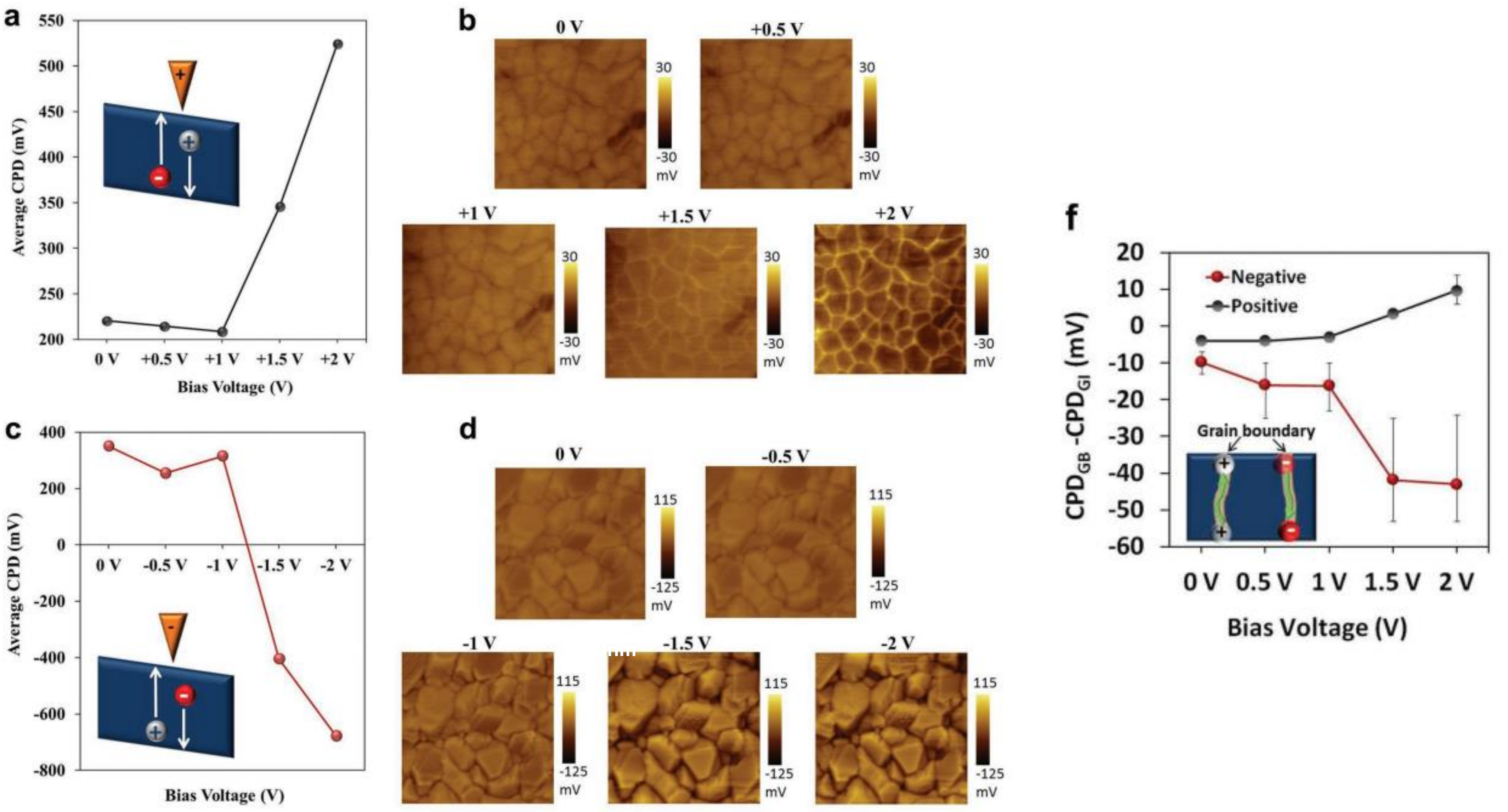
ION MIGRATION IN HALIDE PEROVSKITE



J. Yun et al. Advanced Energy Materials 6 (13), 1600330

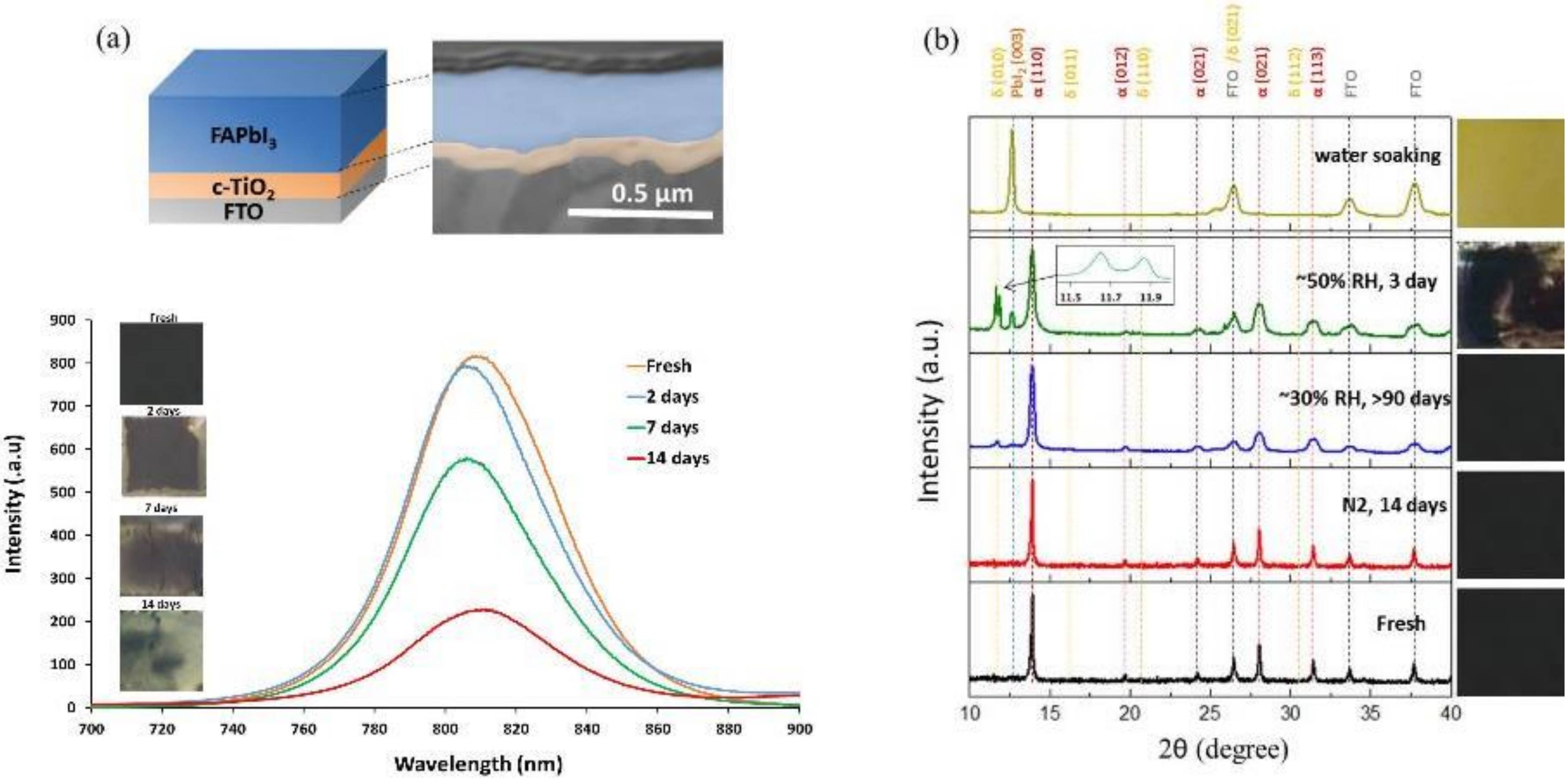
Grain boundaries are inflated due to the ion migration

ION MIGRATION IN HALIDE PEROVSKITE



Grain boundaries act as channels for ion migration

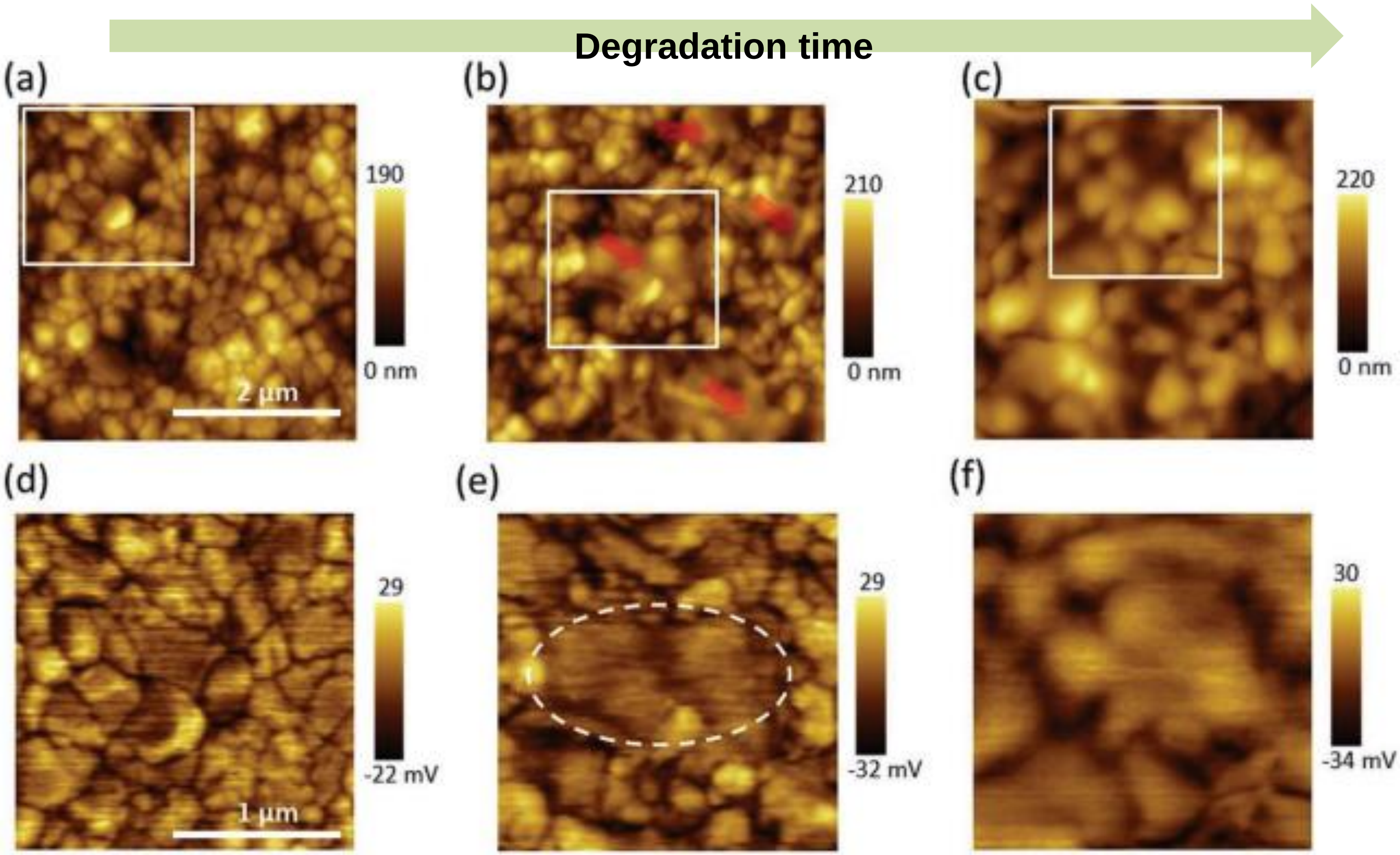
DEGRDATION IN HALIDE PEROVSKITE



J. Yun et al. Advanced Functional Materials 28 (3), 1705363

FAPbI3 Perovskite turn into non-perovskite phase at room temperature

DEGRDATION IN HALIDE PEROVSKITE

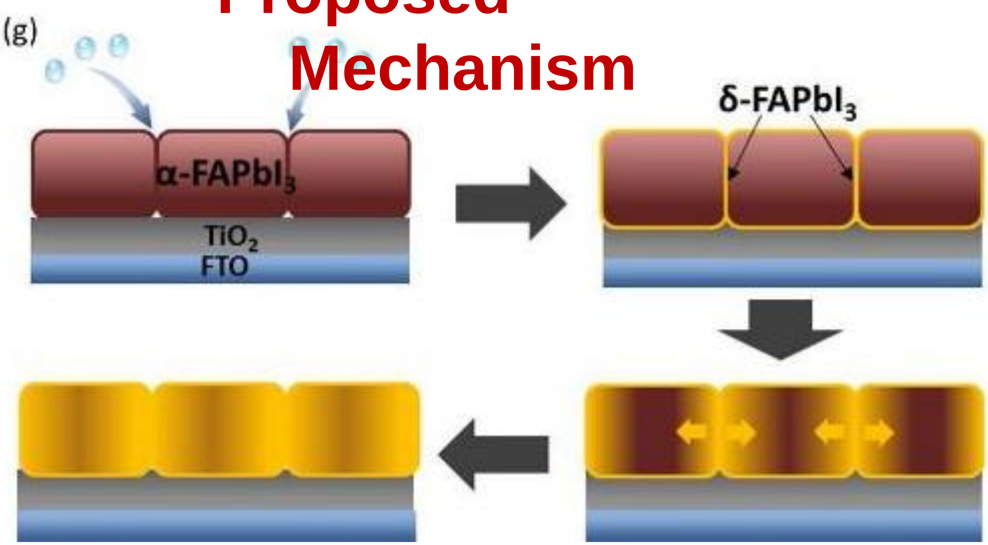


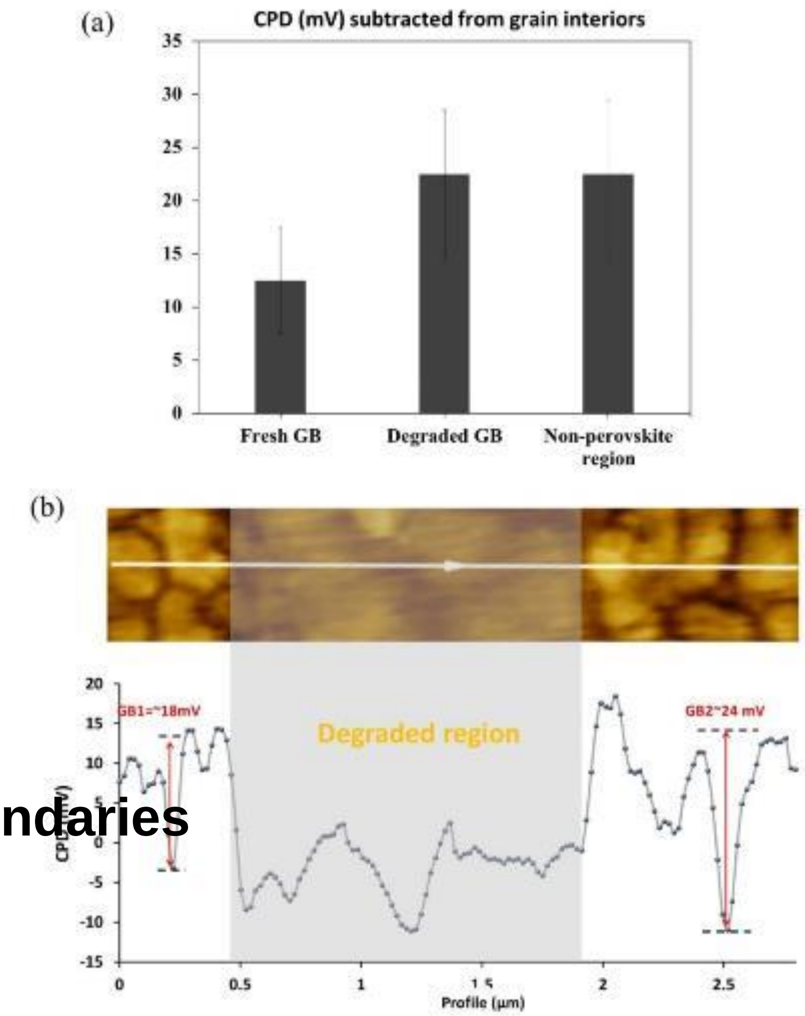
J. Yun et al. Advanced Functional Materials 28 (3), 1705363

Grains merge and grain boundaries become wide and lower CPD

DEGRDATION IN HALIDE PEROVSKITE

Proposed Mechanism

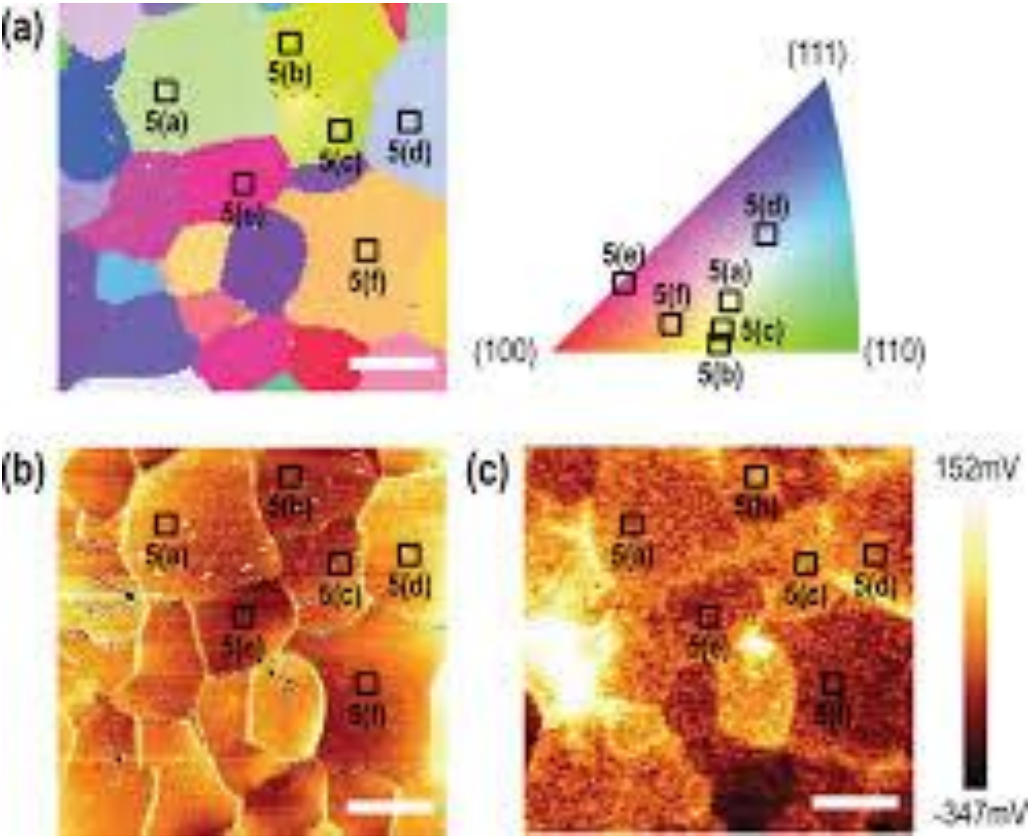




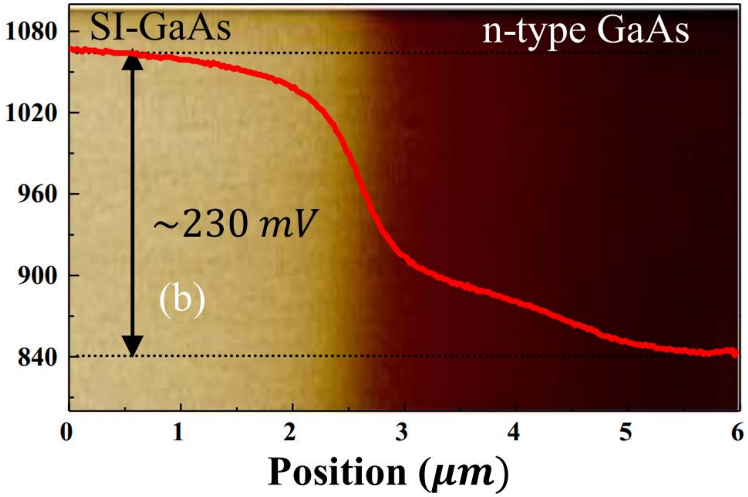
Moisture penetrate through the grain boundaries and yellow phase spreads laterally

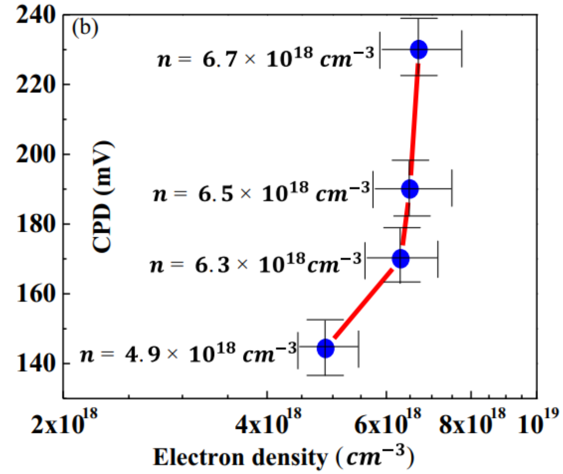
J. Yun et al. Advanced Functional Materials 28 (3), 1705363

OTHER APPLICATIONS



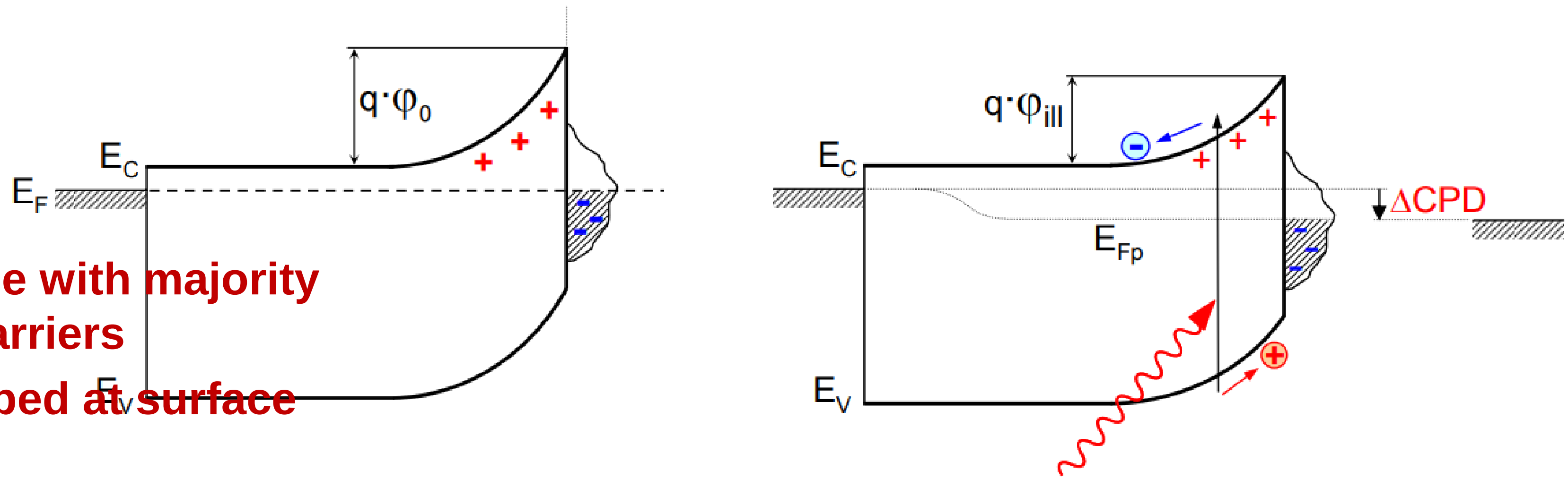
Scientific reports 5 (2015): 8822





Philosophical magazine letters 85.1 (2005): 41-49.

Surface photovoltage= CPD_{light}-CPD_{dark}



n-type with majority carriers trapped at surface

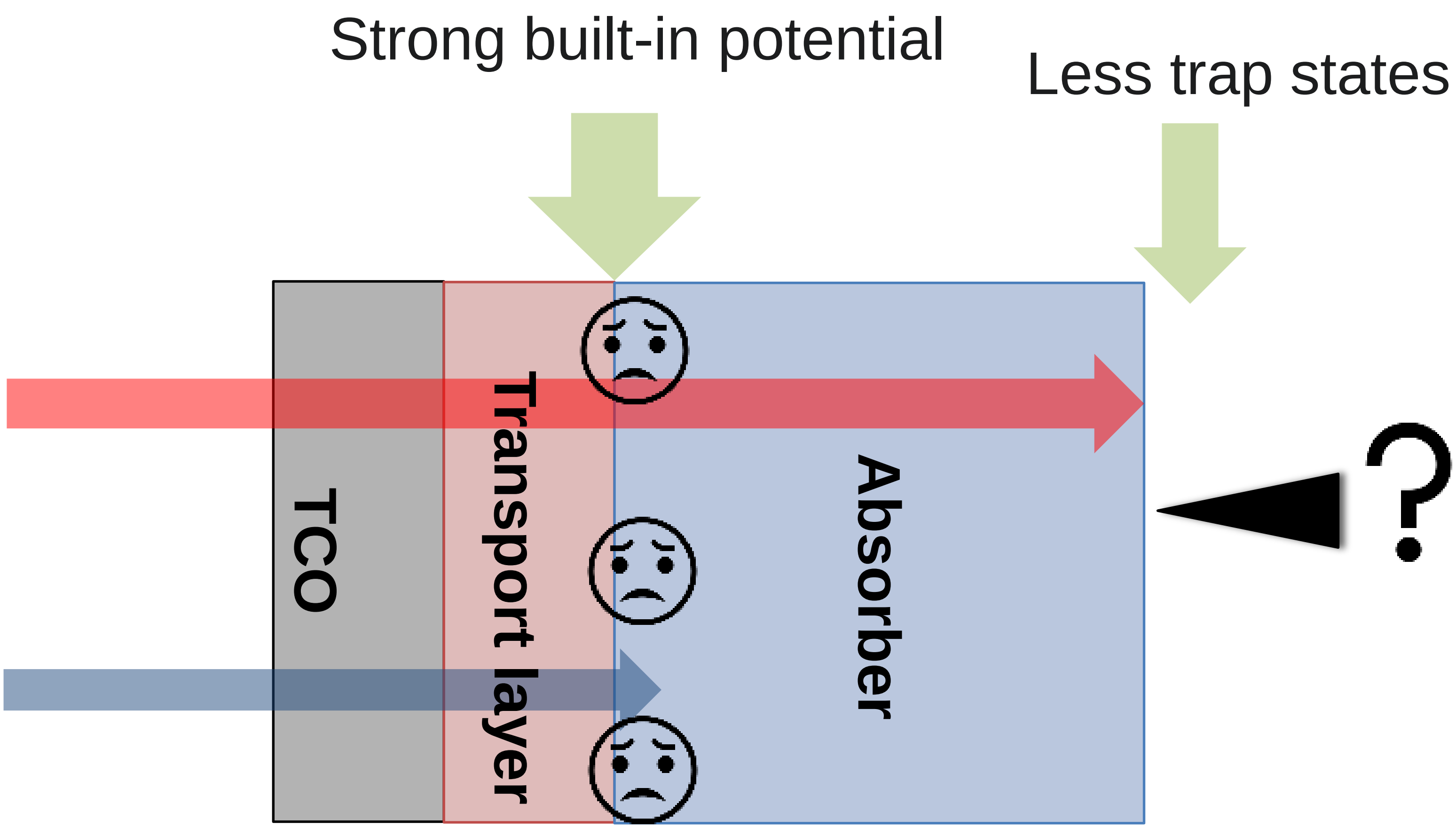
SPV can be expressed by the density of photogenerated charge carriers (Δn = Δ p) and the density of minority charge carriers in thermal equilibrium

Top surface depleted by surface defects? Where is pn junction? What is bandgap?

What is diffusion length?

Lecture by Thoas Dittrich, HZB, 2010

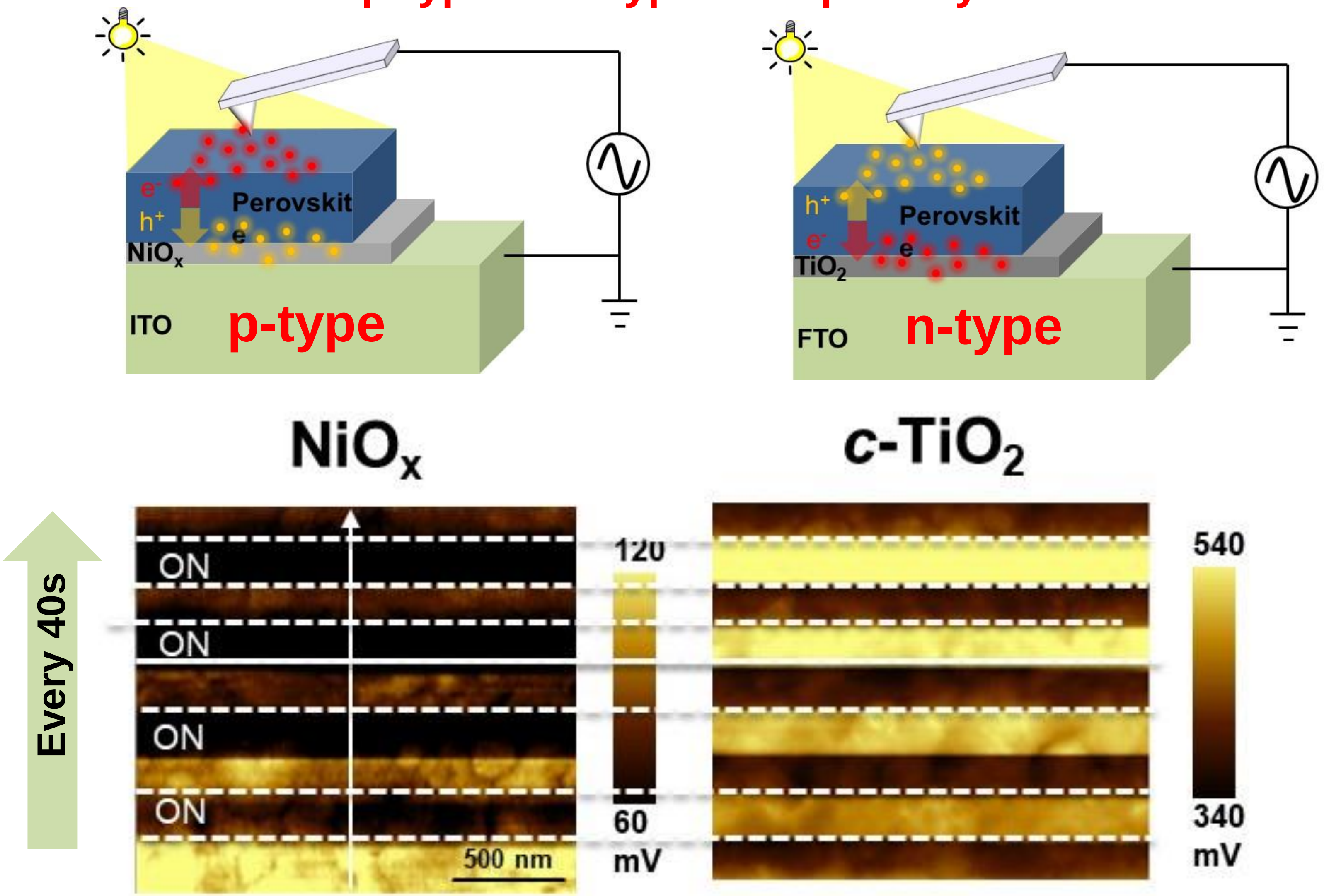
SURFACE PHOTOVOLTAGE



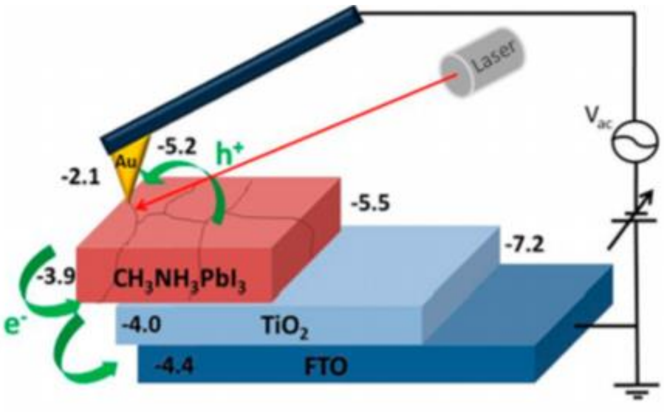
Intensity and wavelength dependent KPFM

SURFACE PHOTOVOLTAGE

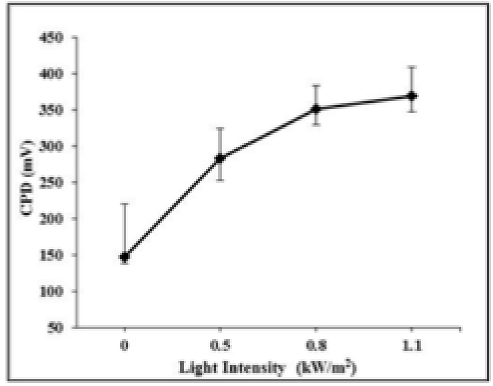
p-type vs n-type transport layer



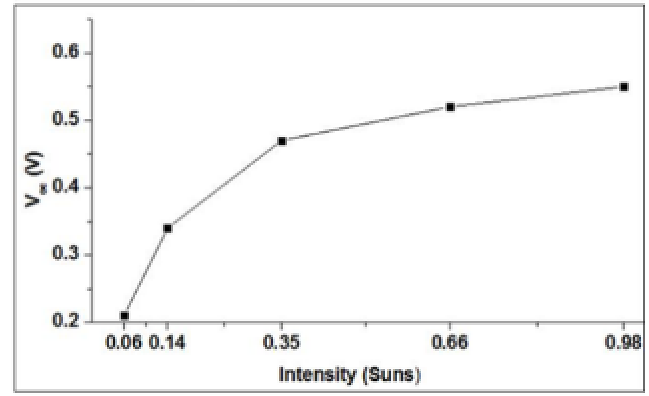
SURFACE PHOTOVOLTAGE



CPD *vs.* Light Intensity



V_{oc} vs. Intensity



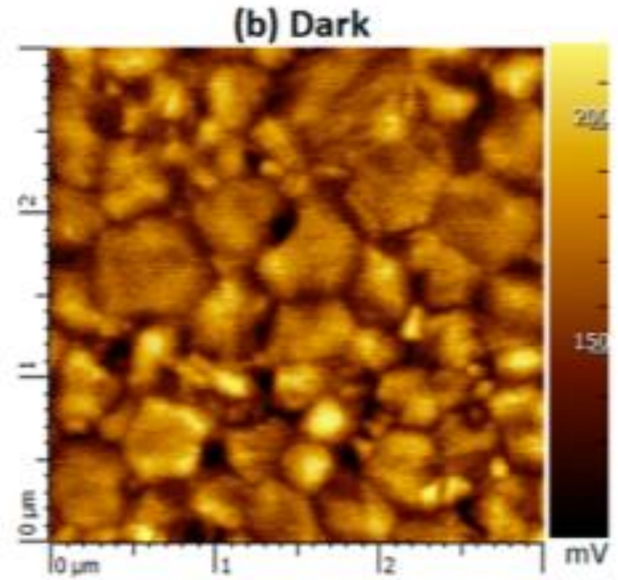
J.Yun et al. The journal of physical chemistry letters 6 (5), 875-880

Sub-linear behavior of contact potential difference and open-circuit voltage

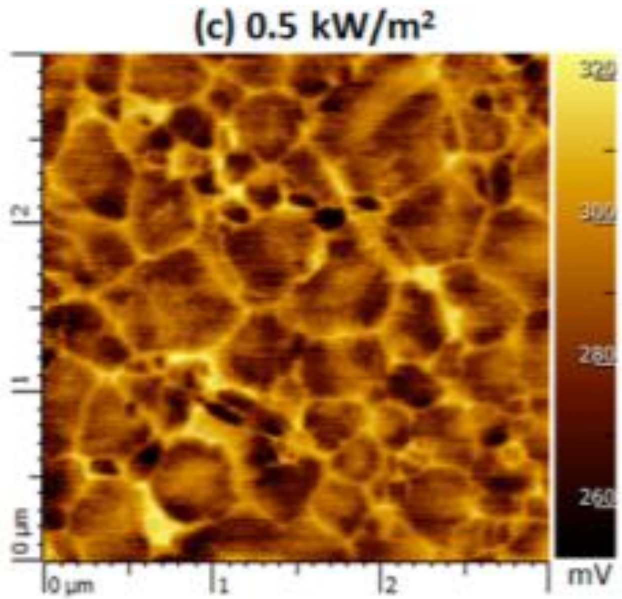
Our obtained CPD can be correlated with the open circuit potential under illumination

GRAIN BOUNDARIES IN HALIDE PEROVSKITES

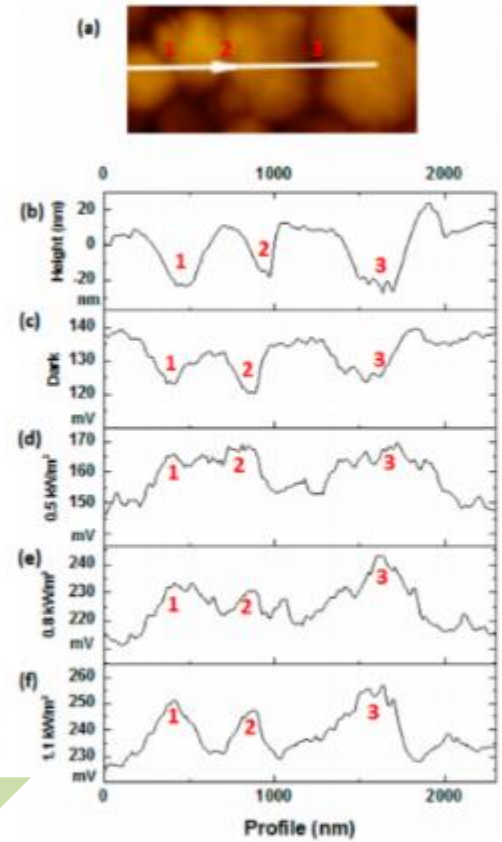
CPD in Dark



CPD in light



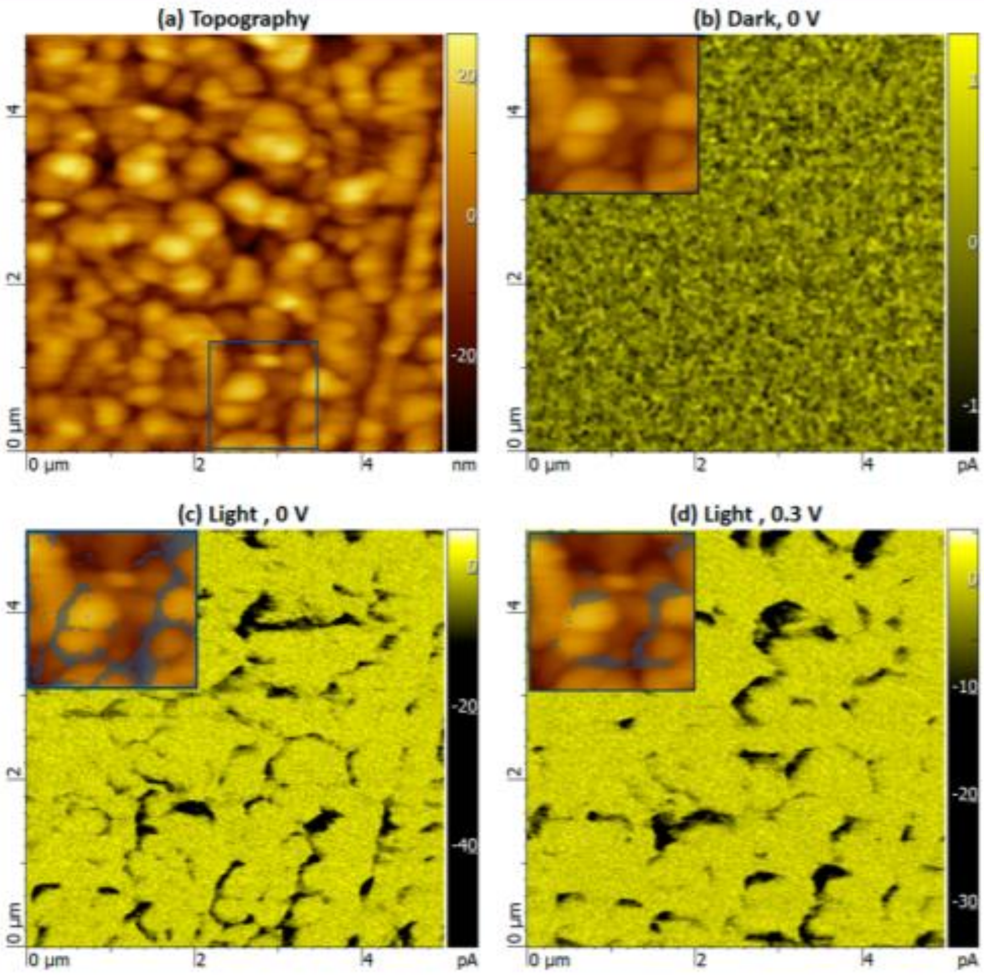
Light Intensity

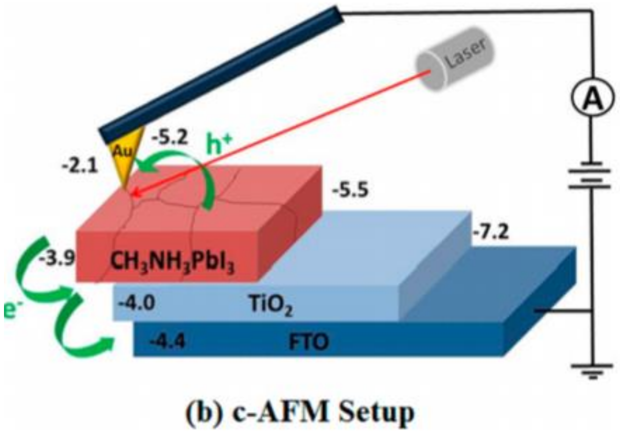


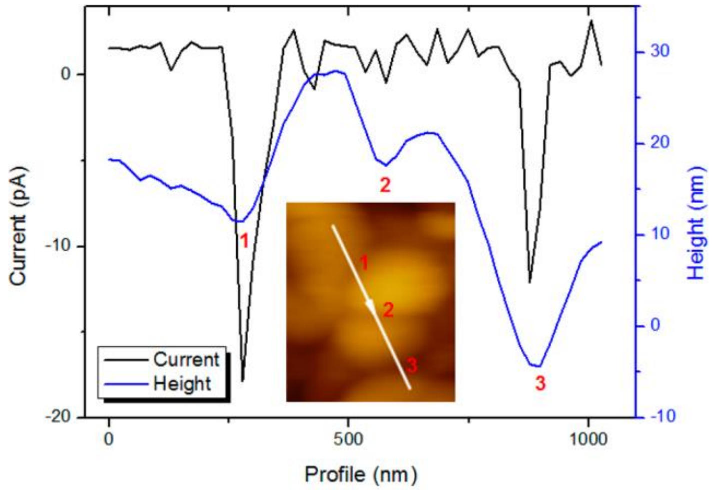
Grain boundaries show higher CPD compare to grain interiors

J.Yun et al. The journal of physical chemistry letters 6 (5), 875-880

PHOTOCURRENT MAPPING



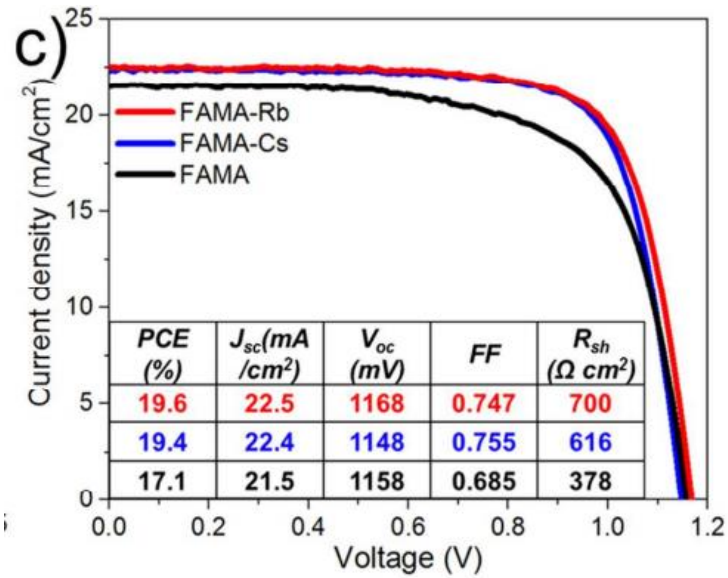




J.Yun et al. The journal of physical chemistry letters 6 (5), 875-880

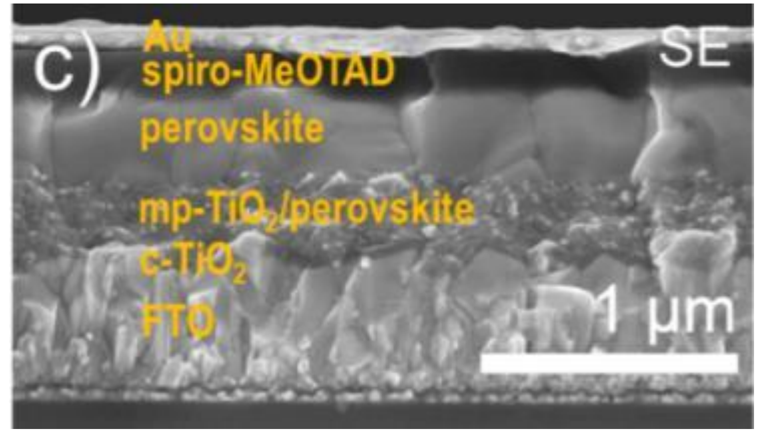
Higher photocurrent at GBs

INORGANIC CATION INCORPORATED PEROVSKITES

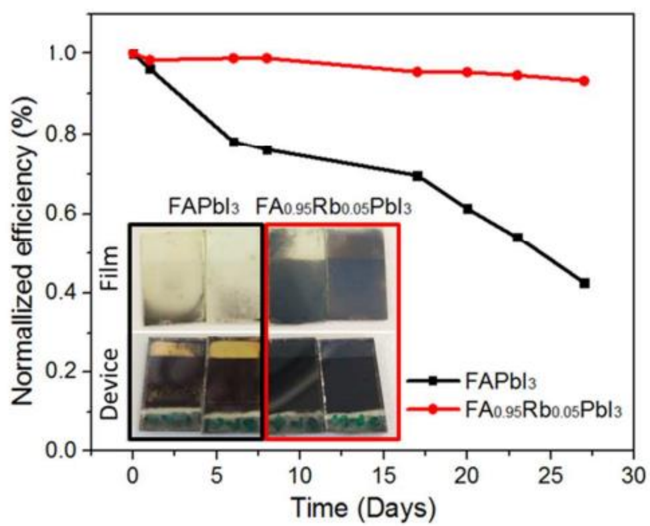


PCE (%)	J_{sc}(mA /cm²)	V_{oc} (mV)	FF	R_{sh} (Ω cm²)
19.6	22.5	1168	0.747	700
19.4	22.4	1148	0.755	616
17.1	21.5	1158	0.685	378

$(FA_xRb_{1-x}PbI_3)_{0.85}(MAPbBr_3)_{0.15}$

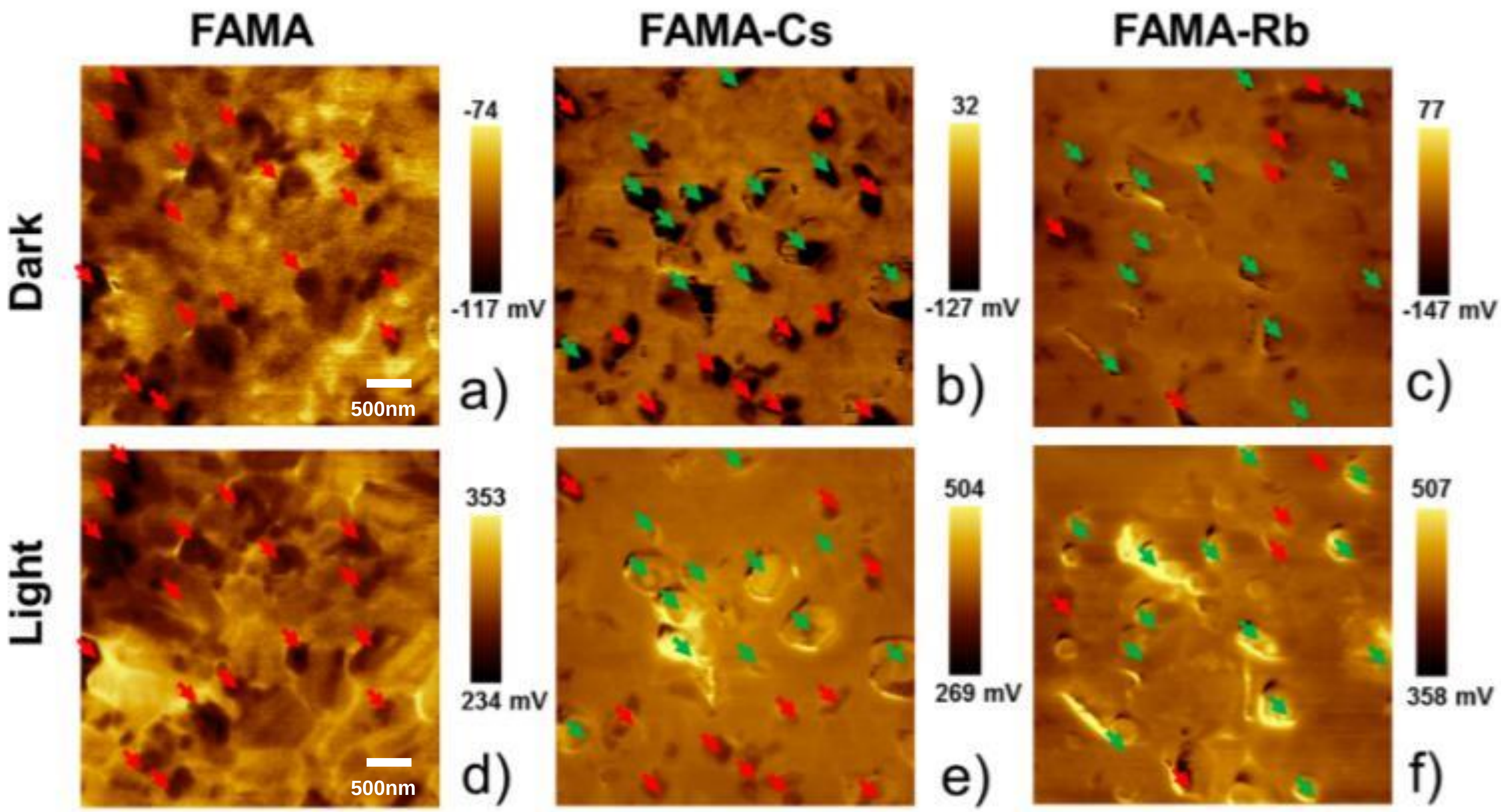


ACS Energy Letters 2 (2), 438-444



Incoporation of Rb improved efficiency and stability

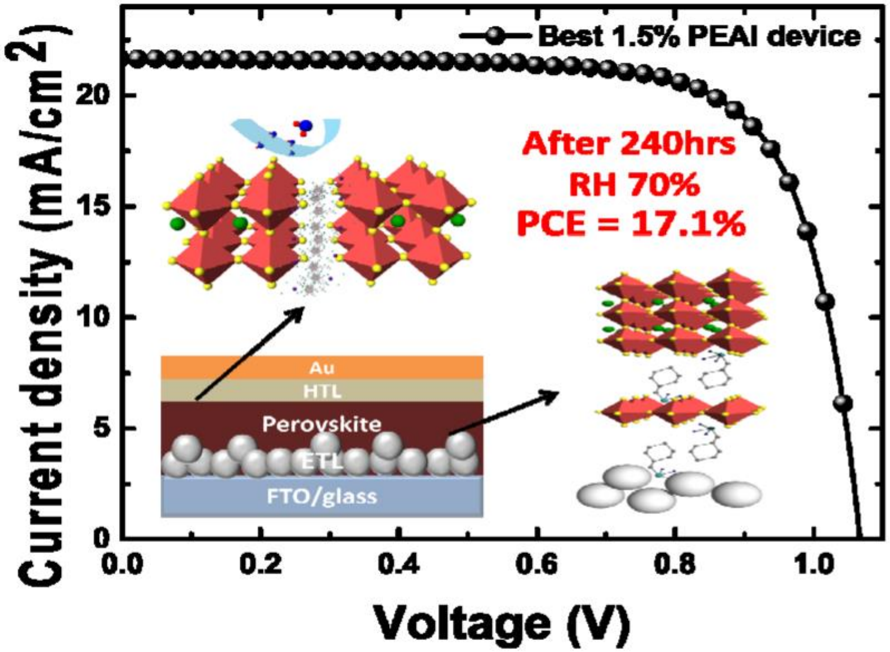
INORGANIC CATION INCORPORATED PEROVSKITES

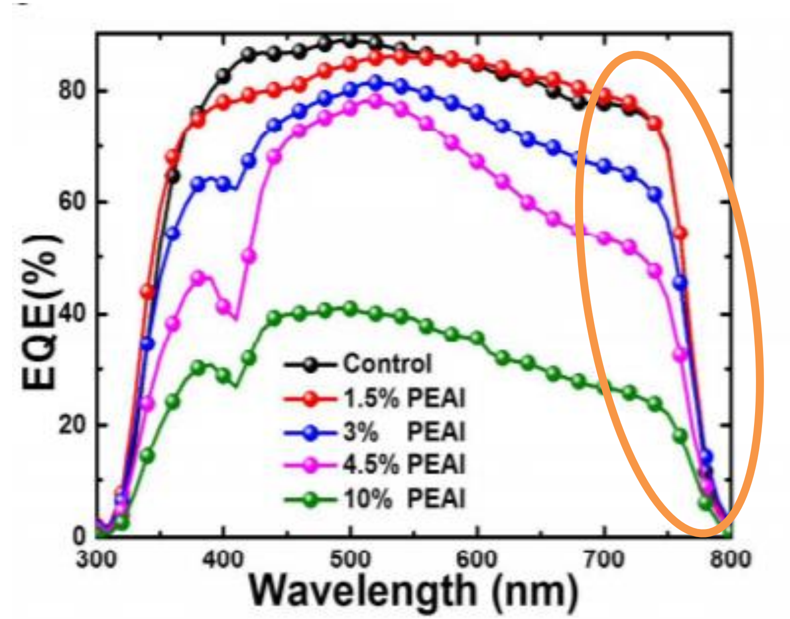


ACS Energy Letters 2 (2), 438-444

Cs and Rb forms nanoclusters and have higher SPV!!

LONG-CHAINED CATION MIXED PEROVSKITES

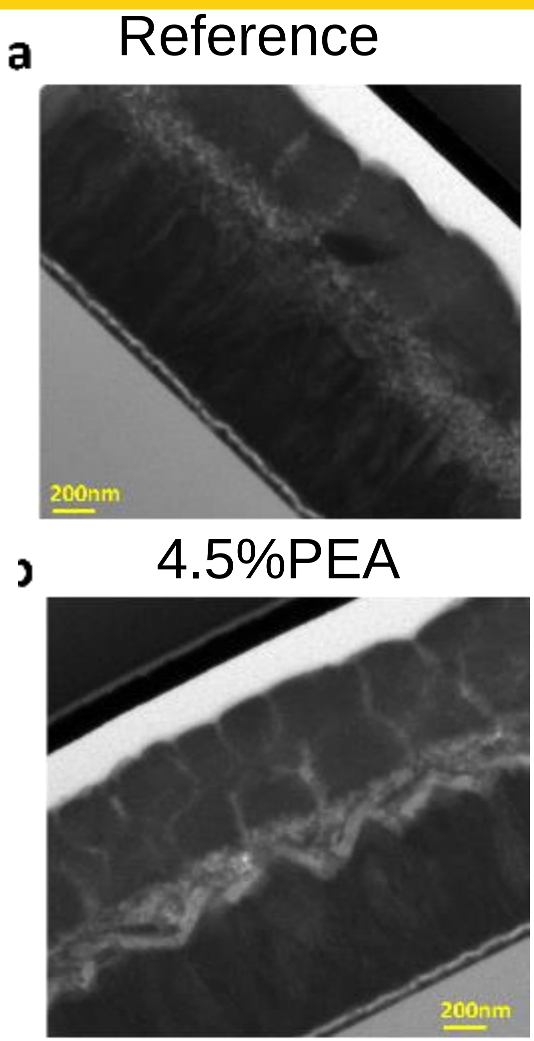


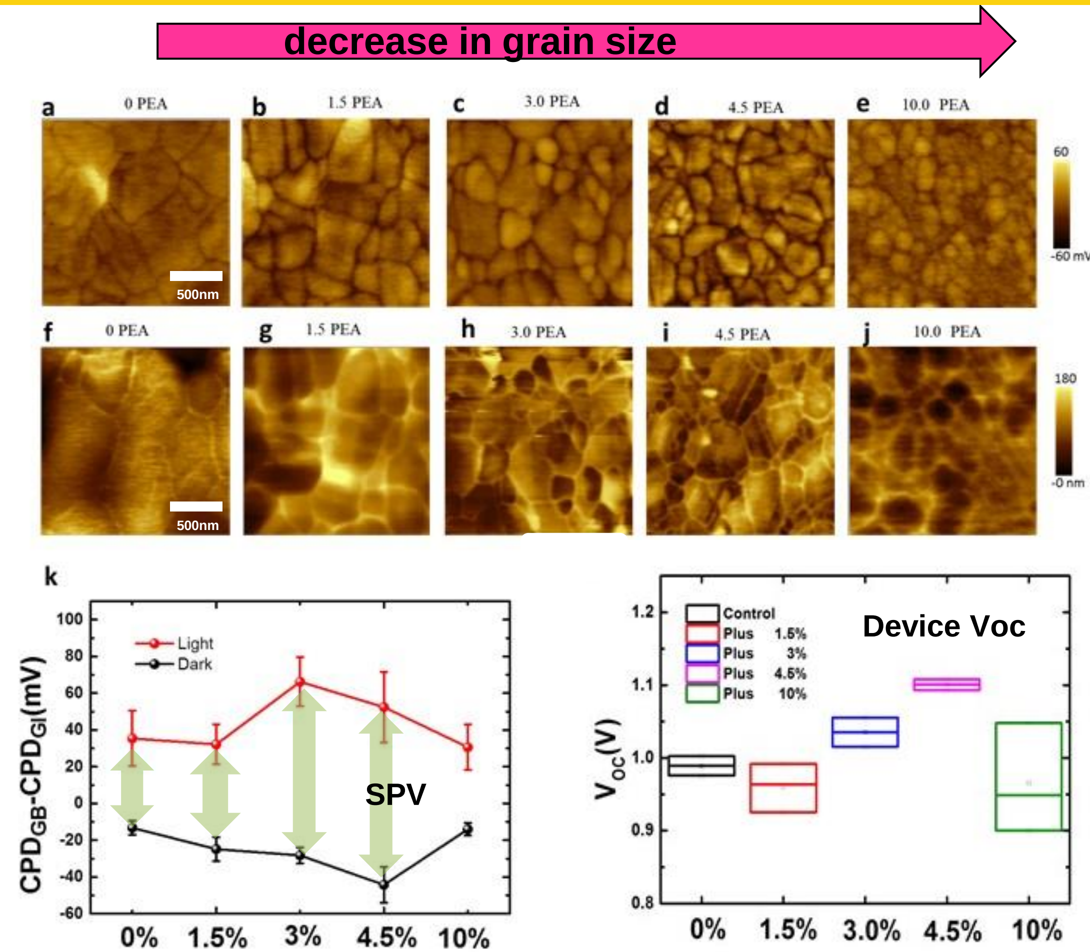


	PEAI	J_{SC}	V_{OC}	FF	PCE
After 1200 hrs.	Control	-64%	-1%	-15%	-71%
	1.5% PEAI	-13%	+7%	-10%	-17%
	3.0% PEAI	1%	-3%	-13%	-15%
	4.5% PEAI	-8%	-9%	-22%	-15%
	10% PEAI	+25%	-1%	18%	52%

ACS Energy Letters 3 (3), 647-654

LONG-CHAINED CATION MIXED PEROVSKITES

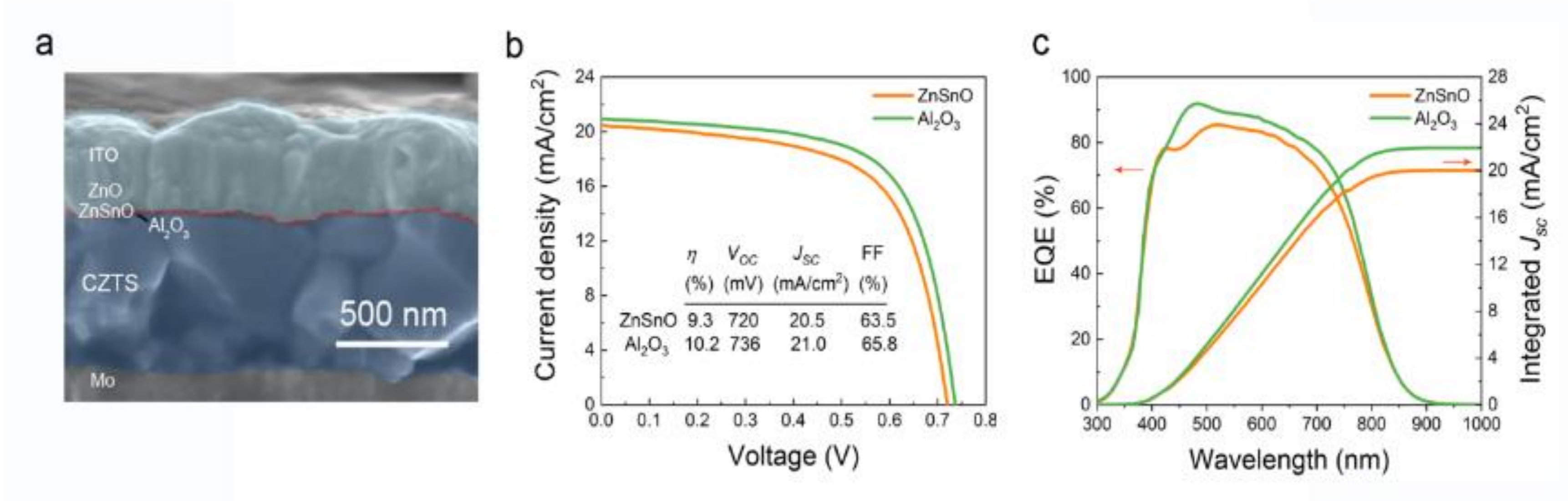




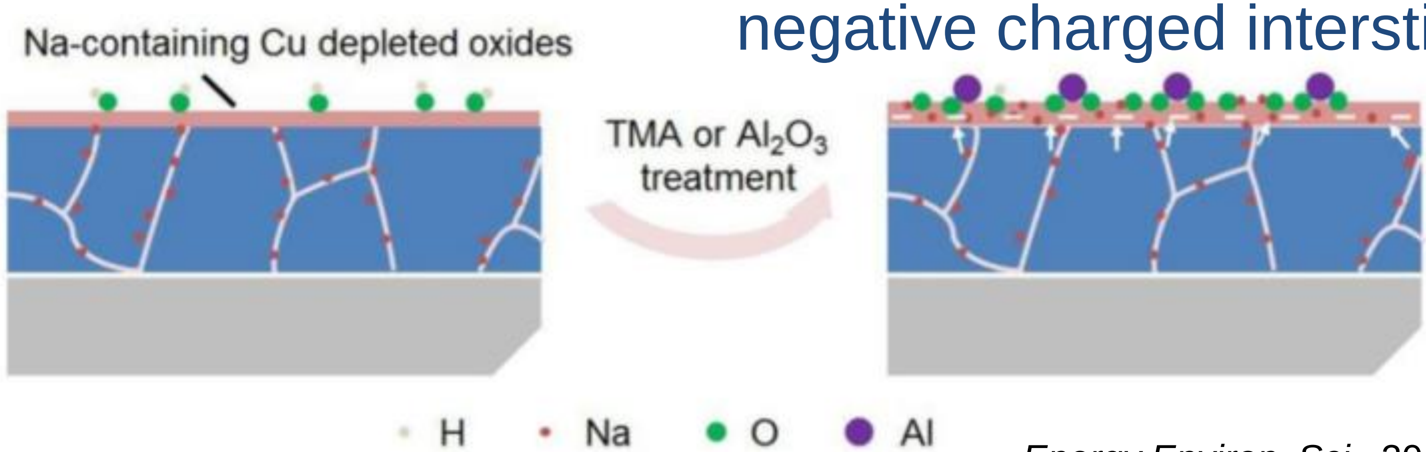
ACS Energy Letters 3 (3), 647-654

Voc↑ with grain size ↓ Enlarged bandgap at the GBs?

ALUMINA PASSIVATED CZTS SOLAR CELLS



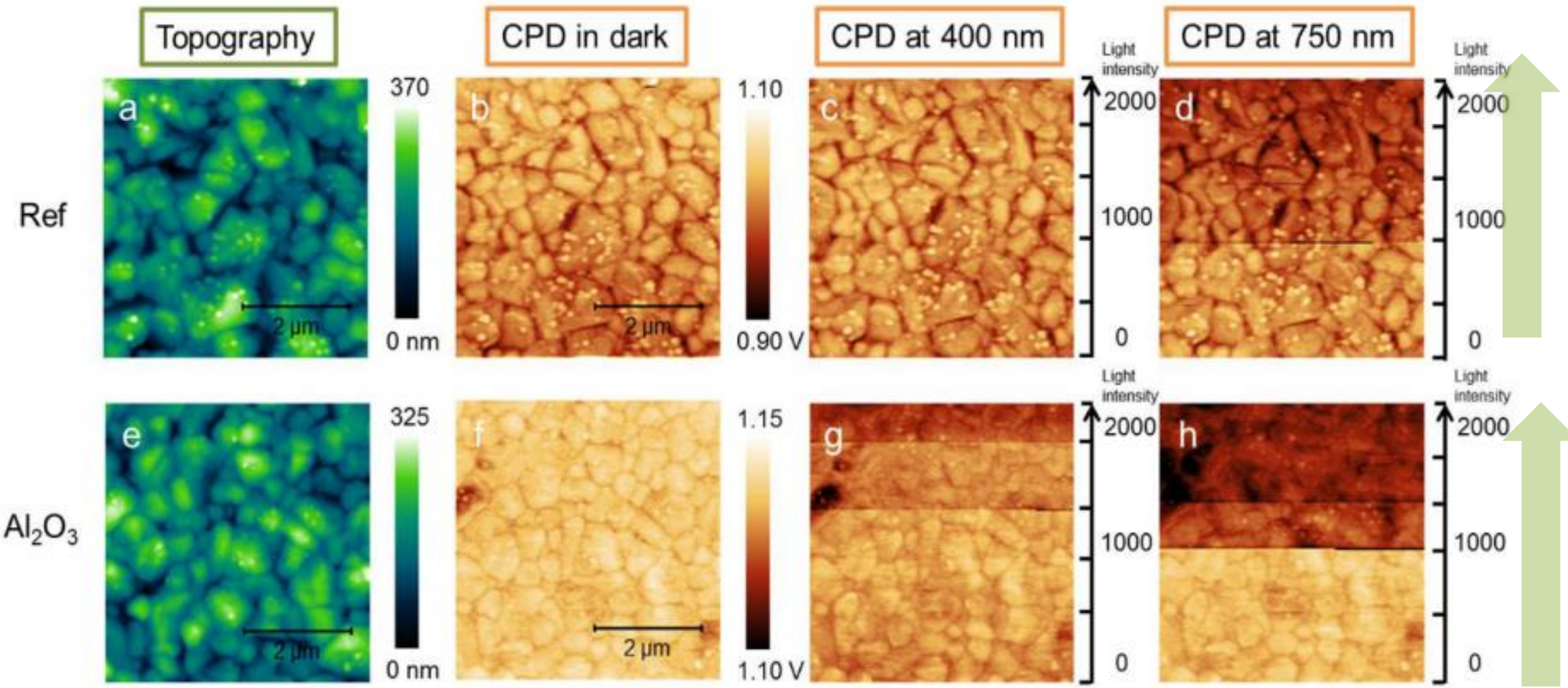
negative charged interstitial O_i^-



Energy Environ. Sci., 2019

Several nm thick Al_2O_3 layer with trimethylaluminum (TMA) precursor enabled over 10% efficiency!

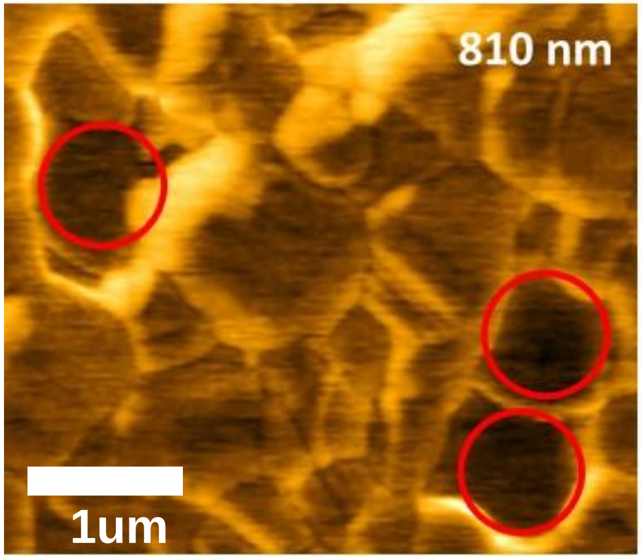
ALUMINA PASSIVATED CZTS SOLAR CELLS

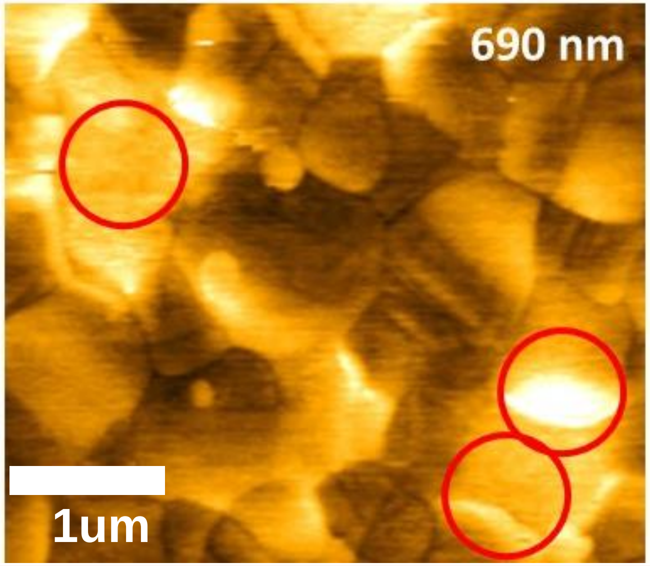


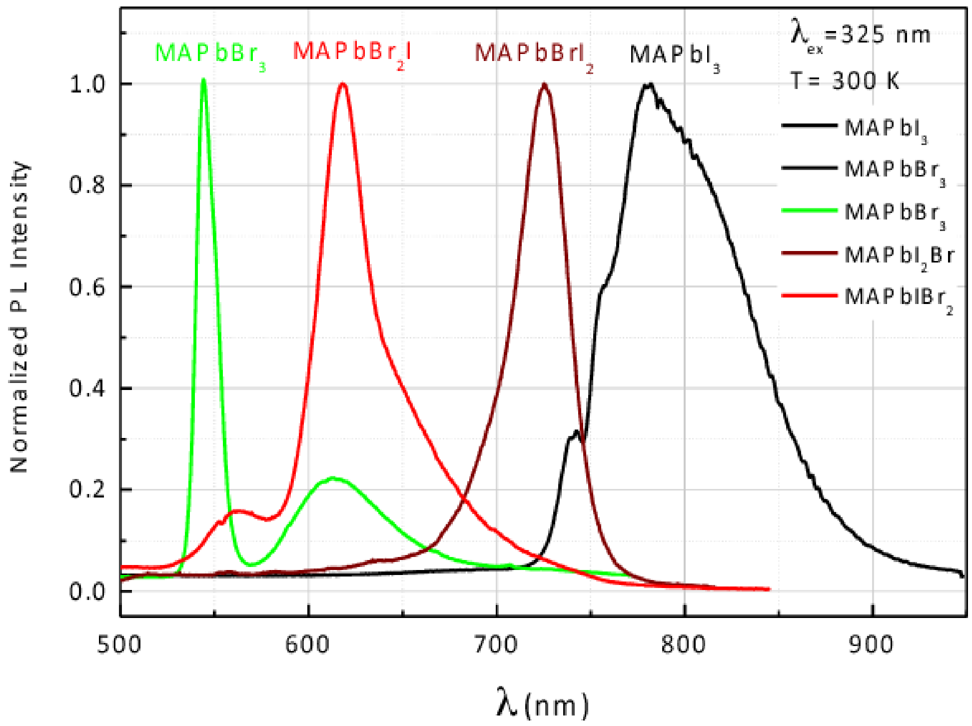
Energy Environ. Sci., 2019

Higher response of CPD at both wavelengths when Al_2O_3 is deposited on top of CZTS

CPD UNDER ILLUMINATION

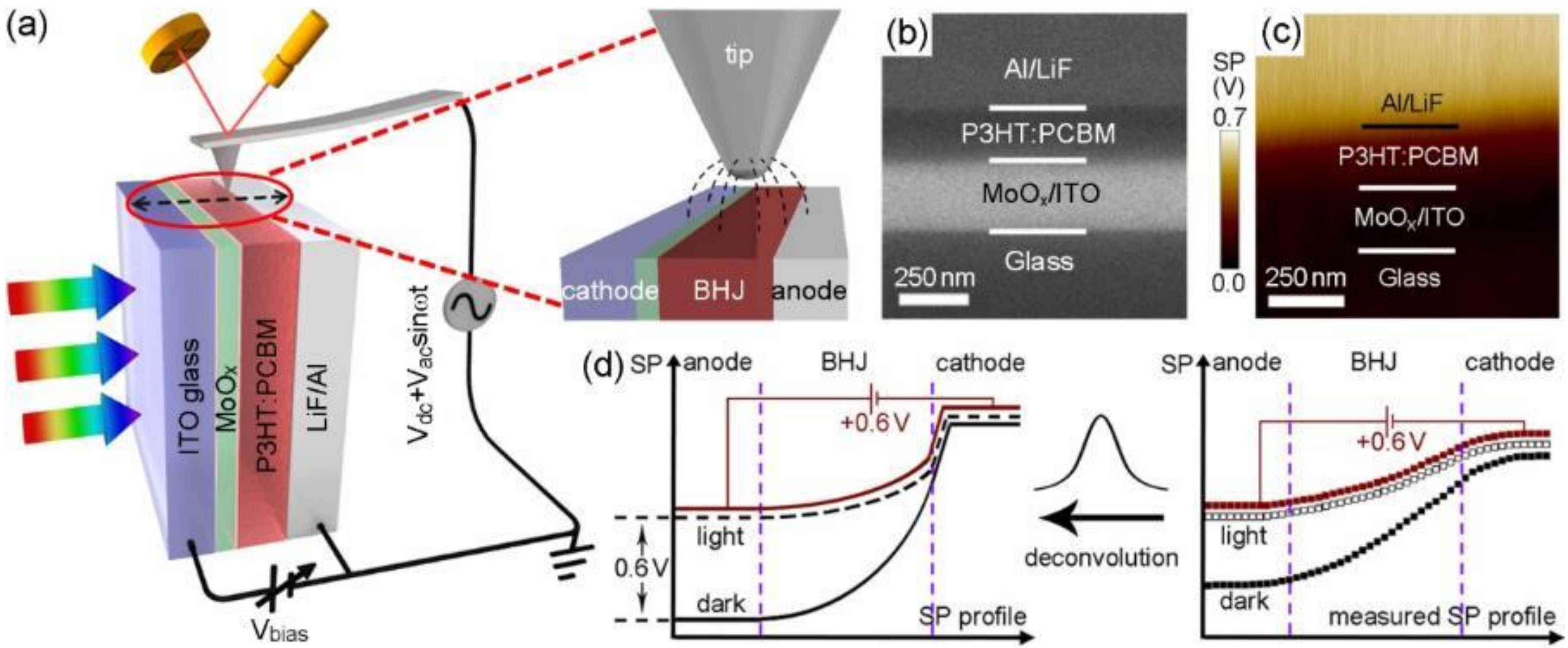






Grain to grain band gap difference from halide segregation

CROSS-SECTION KPFM

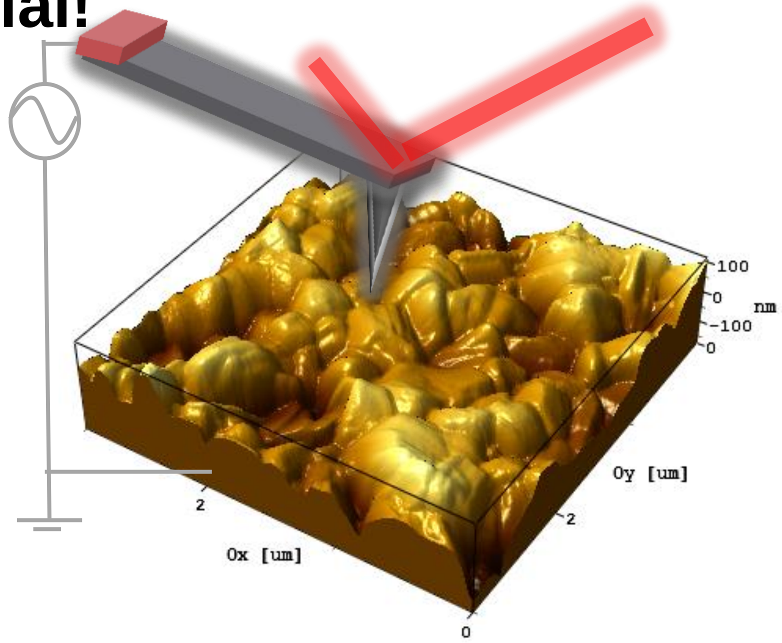


Nature communications 6 (2015): 7745.

pn junction profile, charge transport properties at each interface, and band alignment

SUMMARY

Allows 3D nanoscale mapping of your material!



Work function distribution, ion migration, charge transport, surface photovoltage, pn junction properties, and many more!

WHERE IS AFM?

School of Materials Science

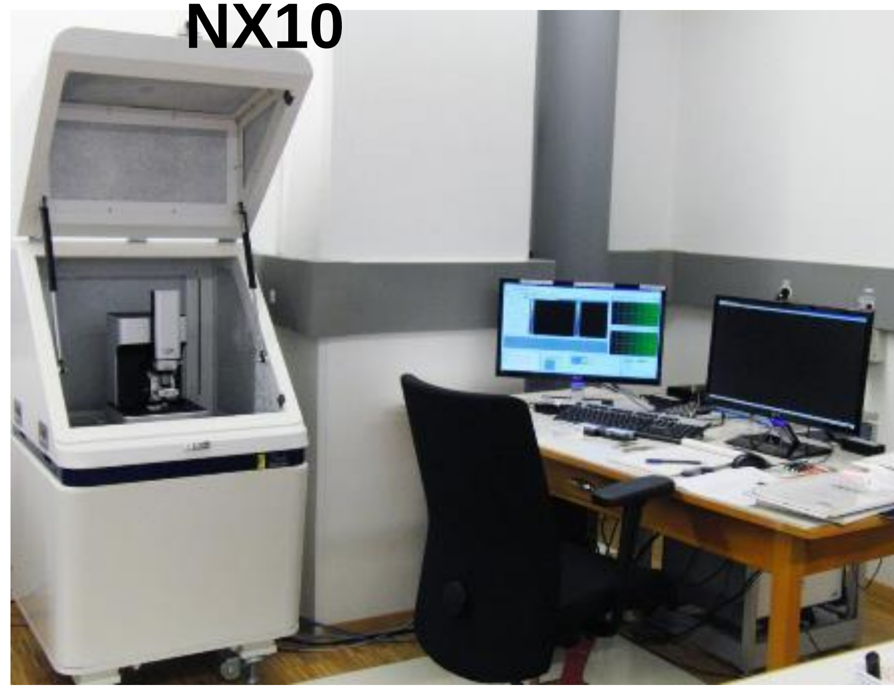
Several AFMs

Prof. Jan Seidel

Humidity control, different environments, temperature control,

tuneable laser, liquid

SPREE- Park System NX10



To be installed soon!

KPFM with LED lights, conductive AFM local

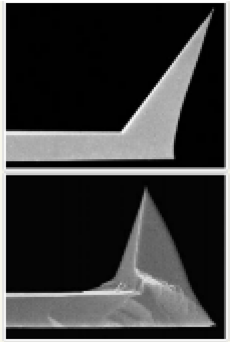
IV curve, EFM, PFM, Phase imaging

FAQS

1. **How long does it take to measure? For instances, 5 x 5 um^2?**
2. **How easy is it obtain a high quality CPD image?**
3. **What type of probe to use?**
4. **What sample roughness is allowed?**

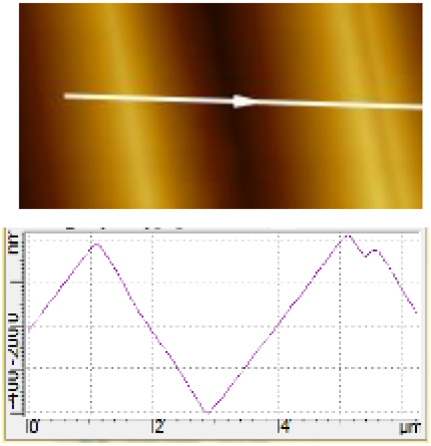
PT-IR COATED PROBES:

- ANSCM series probes are silicon probes coated with Pt-Ir on both sides for EFM applications.
- Available as ANSCM-PC, ANSCM-PT and ANSCM-PA probes for Contact, Force modulation and Tapping™/Non-contact EFM applications, respectively.
- ACCESS (tip view) probes coated with Pt-Ir (ACCESS-EFM) for contact/force modulation mode EFM applications.

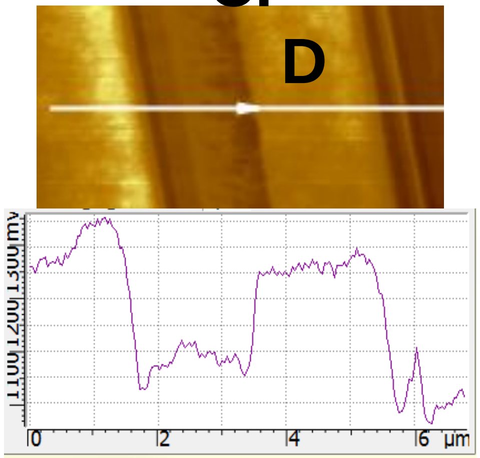


Parameter	ANSCM-PC	ANSCM-PT	ANSCM-PA	ANSCM-PA5	ACCESS-EFM
k (N/m)	0.2	3	40	40	2.7
f (kHz)	12	60	300	300	60
Length	450	225	125	125	245
Width (µm)	40	46	35	35	52
Thickness (µm)	2.5	2.5	4.5	4.5	2.8
Tip ROC (nm)	30	30	30	55	30
Ptlr thickness (nm)	25±5	25±5	25±5	50±5	25±5

Height



CPD



Acknowledgement

Thanks to

Ziv, Jessica, Ned, Jeana, Shujuan,

Stephen for their contribution!

Of course, SPREE and SPREE people!

Special thanks to:

Martin Green (UNSW)

Jan Seidel (UNSW)

Thanks to my collaborators:

Sang Il Seok (UNIST)

Jincheol Kim (KETI)

Dohyung Kim (Tennessee University)

Jun Hong Noh (Korea University)

Jeana Hao (UNSW)

Anita Ho-Baillie (UNSW)

Shujuan Huang (UNSW)

Jangwon Seo (KRICT)

Jung Ho Yun (UQ)

And many others