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

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MOTIVATION

Crystalline Si thin film on Glass (CSG) Technology

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

“Spatial resolution of few tenth of nanometre is required”

“Atomic interaction between tip and the sample”
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

1st pass → Height
2nd pass → CPD

Imaging height signal and CPD signal at the same spot!


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An **electrostatic force** exists between tip and sample due to work function difference and **DC voltage** is applied to **nullify** the force. **>1 nm and >1 mV spatial resolution**
CPD measures **work function of a sample surface**

**What does this mean to us?**

*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.

Advanced Energy Materials 8 (23), 1701940
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CONTACT POTENTIAL DIFFERENCE (CPD)

Iodide vacancies in halide perovskite changes work function

J. Yun et al. Advanced Energy Materials 6 (13), 1600330
Nature Communications 6, 7497 (2015)
ION MIGRATION IN HALIDE PEROVSKITE

Grain boundaries are inflated due to the ion migration

J. Yun et al. Advanced Energy Materials 6 (13), 1600330
Grain boundaries act as channels for ion migration
FAPbI₃ Perovskite turn into non-perovskite phase at room temperature

J. Yun et al. Advanced Functional Materials 28 (3), 1705363
Grains merge and grain boundaries become wide and lower CPD

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

**Surface photovoltage** $= \text{CPD}_{\text{light}} - \text{CPD}_{\text{dark}}$

SPV can be expressed by the density of photogenerated charge carriers ($\Delta n = \Delta p$) 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

Strong built-in potential

Less trap states

Intensity and wavelength dependent KPFM
SURFACE PHOTOVOLTAGE

p-type vs n-type transport layer

Every 40s

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

CPD in light

Grain boundaries show higher CPD compare to grain interiors

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

J. Yun et al. The journal of physical chemistry letters 6 (5), 875-880
Incorporation of Rb improved efficiency and stability

\[(\text{FA}_x\text{Rb}_{1-x}\text{PbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}\]

ACS Energy Letters 2 (2), 438-444
Cs and Rb forms nanoclusters and have higher SPV!!

ACS Energy Letters 2 (2), 438-444
LONG-CHAIN CATION MIXED PEROVSKITES

Current density (mA/cm²)

Voltage (V)

After 240hrs
RH 70%
PCE = 17.1%

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<th>V_OC</th>
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ACS Energy Letters 3 (3), 647-654
LONG-CHAINED CATION MIXED PEROVSKITES

a) Reference

4.5%PEA

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

ACS Energy Letters 3 (3), 647-654
Several nm thick $\text{Al}_2\text{O}_3$ layer with trimethylaluminum (TMA) precursor enabled over 10% efficiency!
ALUMINA PASSIVATED CZTS SOLAR CELLS

Higher response of CPD at both wavelengths when Al₂O₃ is deposited on top of CZTS

Energy Environ. Sci., 2019

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CPD UNDER ILLUMINATION

Grain to grain band gap difference from halide segregation

810 nm

MAP $\text{Br}_3$

MAP $\text{Br}_2$

MAP $\text{Br}_1$

MAP $\text{I}_3$

$\lambda_{\text{ex}} = 325$ nm

$T = 300$ K

Normalized P. L. Intensity

$\lambda$ (nm)

1um

690 nm

1um
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

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FAQS

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