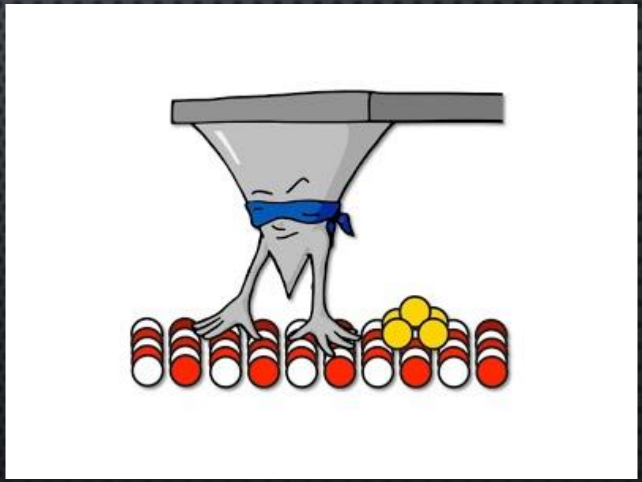
Scanning Probe Microscopy

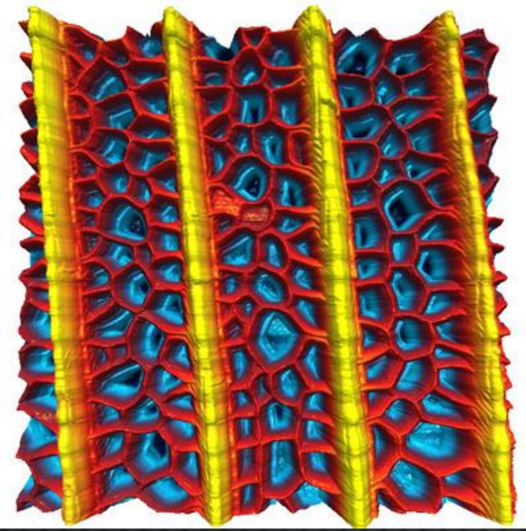
Peggy Zhang

The University of New South Wales
ARC Centre of Excellence in Future Low-Energy Electronics Technologies

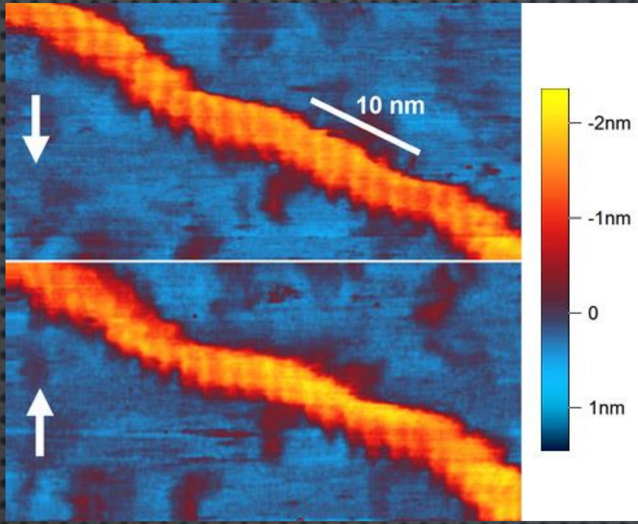
SCANNING PROBE MICROSCOPE (SPM)

“ I can’t see it, but my SPM probe can ! ”

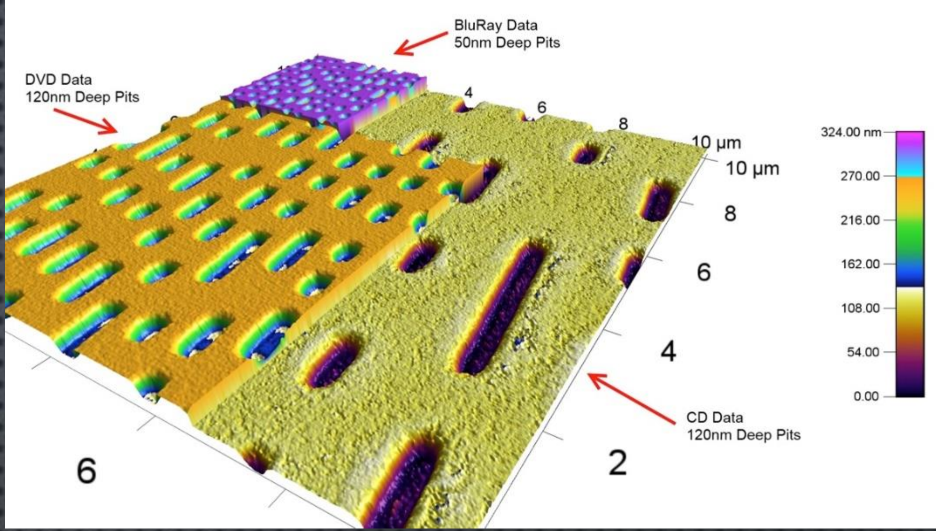




Moth wing

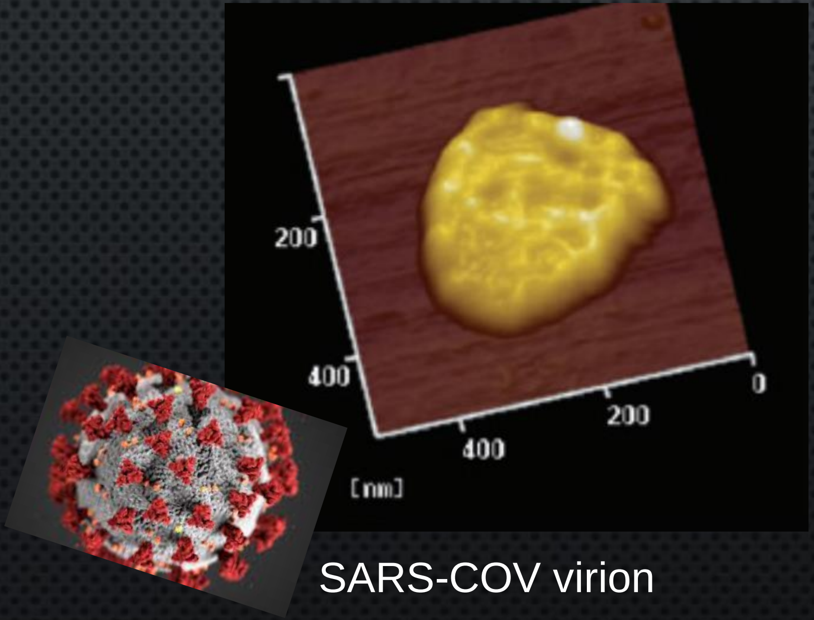


DNA



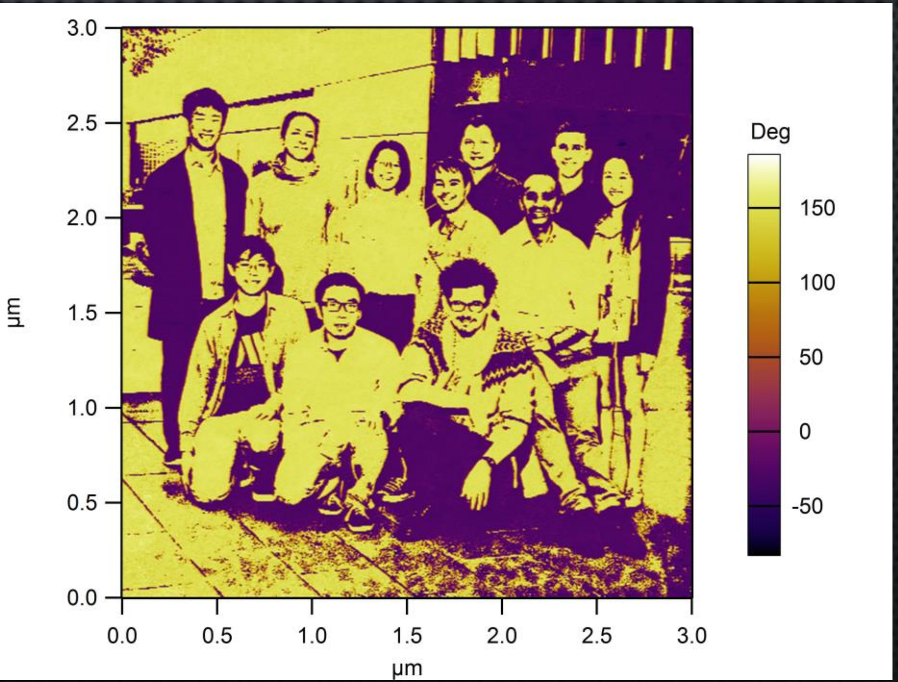
CD/DVD/Blu-ray

----Source: Asylum Research gallery



SARS-COV virion

Cellular Microbiology (2005) 7(12), 1763–1770



Advanced film group

Bismuth ferrite thin films

MANIPULATION

AND

CHARACTERIZATIONS

Scanning Probe Microscopy (SPM)

- **Atomic force microscopy (AFM):**
  -Topography, force measurement

- **Piezoresponse force microscopy (PFM):**
  -Ferroelectric domain structure, domain switching behavior
  Magnetic force microscopy (MFM):
  -Magnetic domain structure

- **Conductive AFM (C-AFM):**
  -Materials conductivity

- **Electrostatic force microscopy (EFM): surface charge**
  Kevin probe force microscopy (KPFM): surface potential, work function, etc.

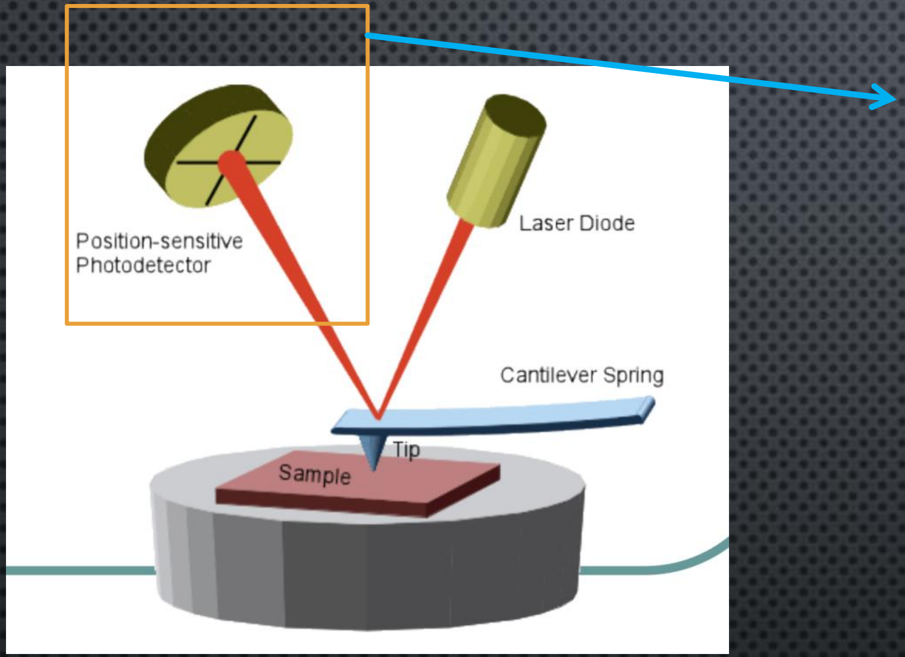
- **Tomographic atomic force microcopy (TAFM)**

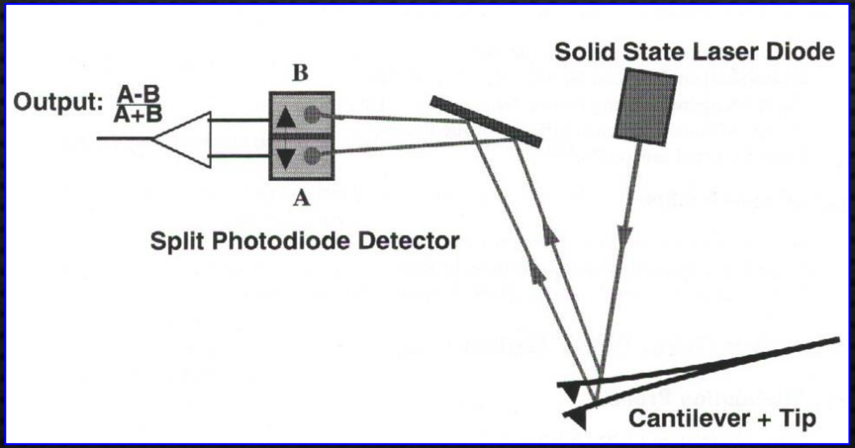
IN-SITU CHARACTERIZATION

- *Temperature control*
- *Atmosphere*
- *Liquid environment*
- *Force*
- Electric field

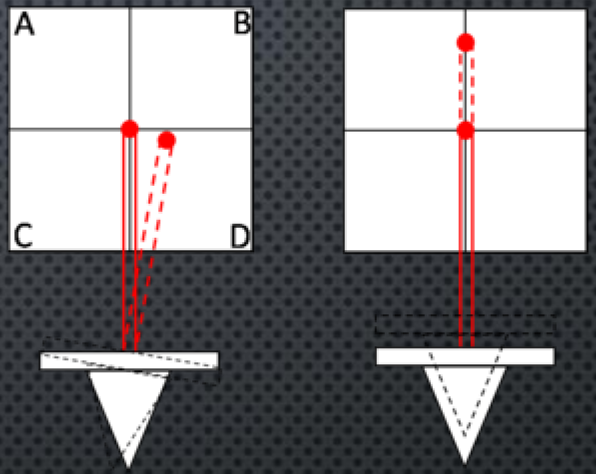
SCANNING PROBE MICROSCOPE

Photodiode detector



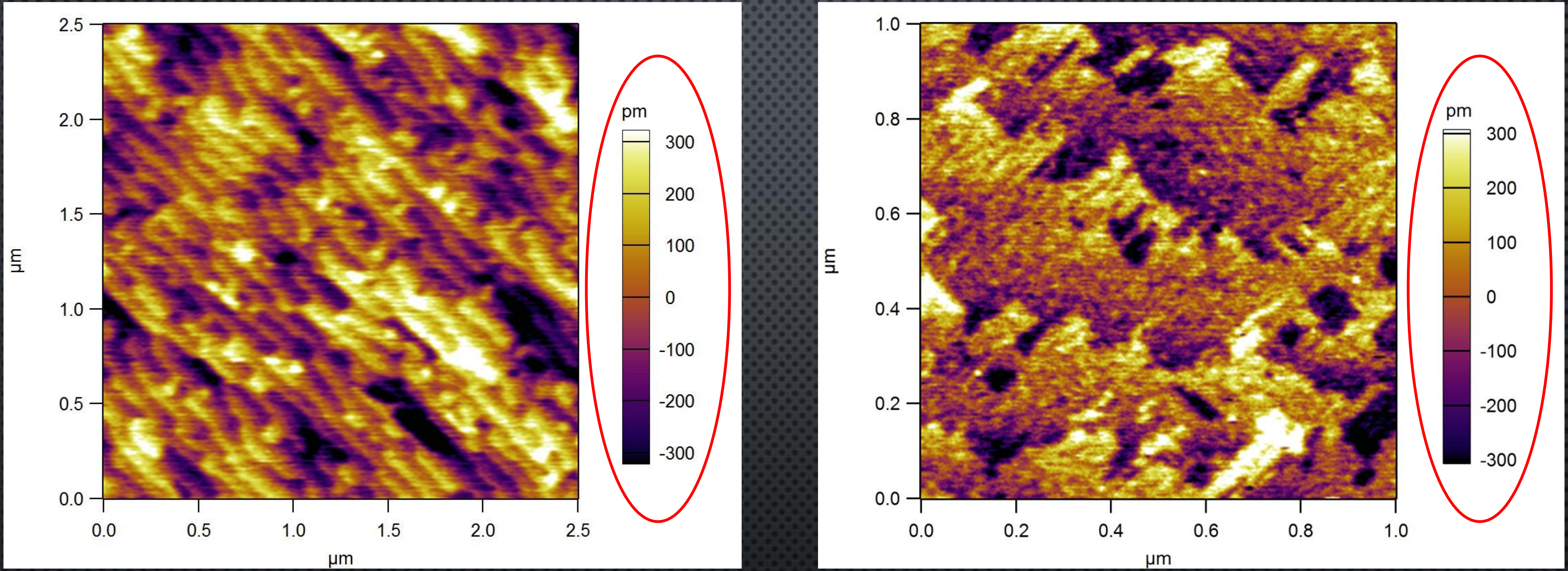


Deflection



- *There are four photodiode component: A, B, C, and D*
- *The sum value is A+B+C+D*
- *A vertical deflection: (A+B)-(C+D)*
- *Similarly a lateral deflection: (B+D)-(A+C)*

TOPOGRAPHY



Roughness in picometer resolution

- ***Morphology***
- ***Thickness***
- ***Roughness***
- ***Defects***

Atomic Force Microscopy

Contact mode

Cantilever maintain a constant deflection:

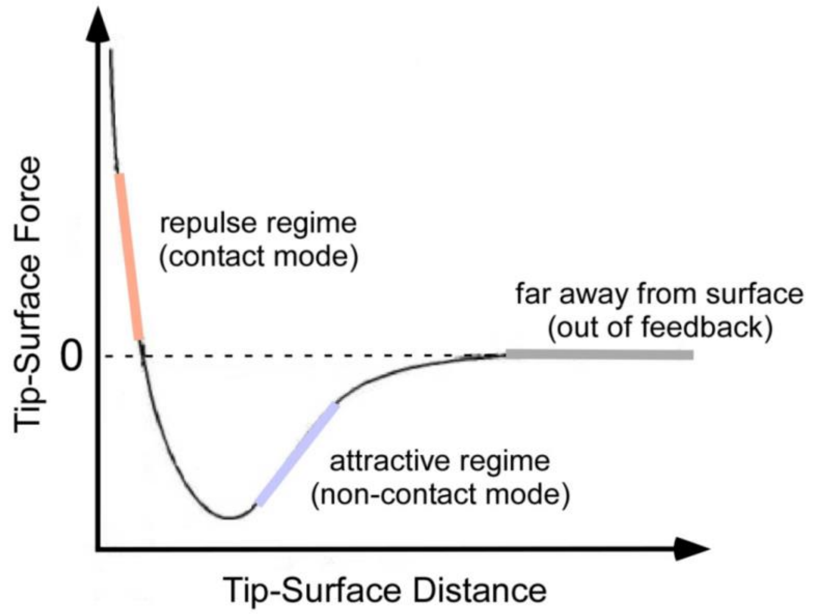
$$F=kx$$

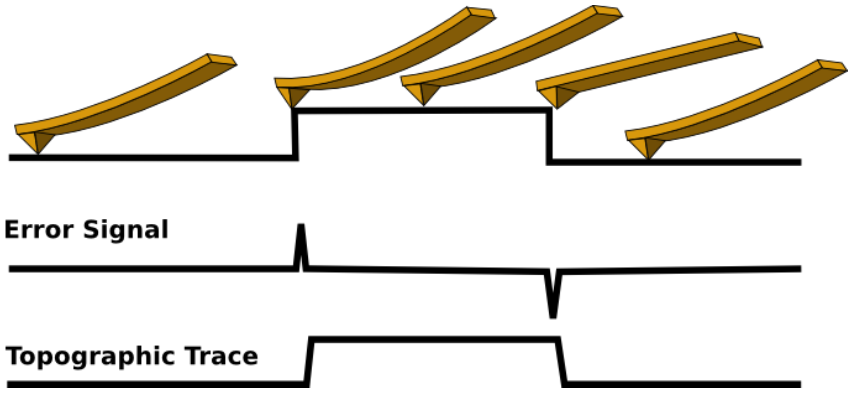
Thus, force also remains constant

Then, the distance the scanner moves in z direction at each point is stored by the computer.

http://www.eng.utah.edu/~lzang/images/Lecture_10_AFM.pdf

http://www.freesbi.ch/en/illustration/figures

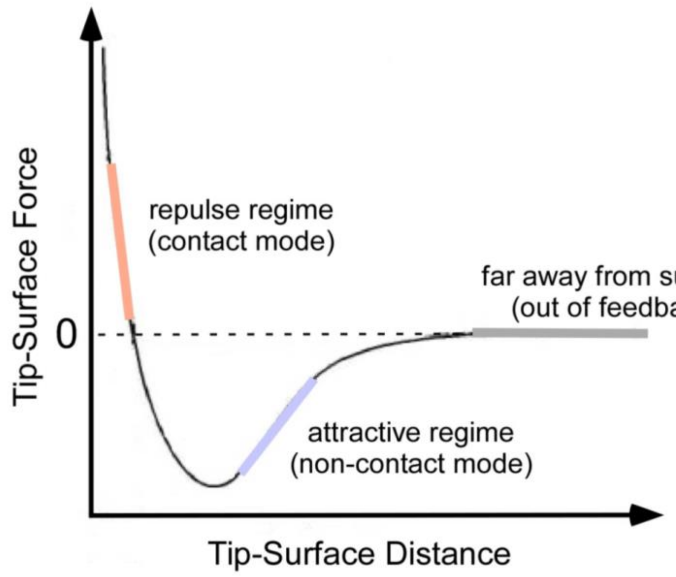


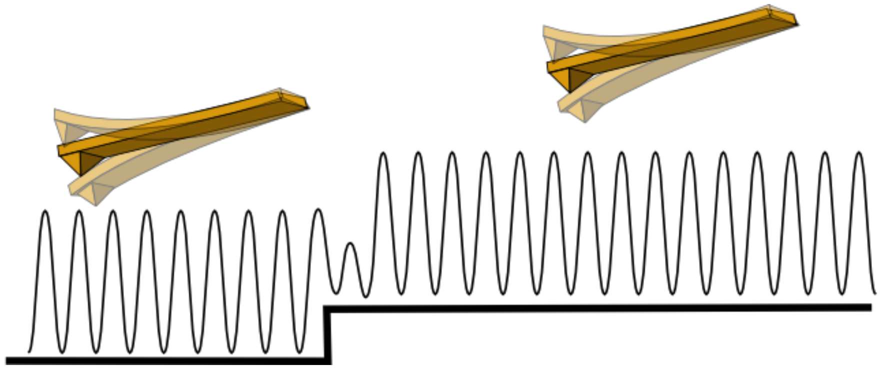


Atomic Force Microscopy

Tapping mode

- *The cantilever is oscillated at or near its resonance frequency*
- *Maintains a constant oscillation amplitude*
- *Vertical position in order to maintain a constant "set point" amplitude*
- *Less destructive, good for soft, fragile materials*

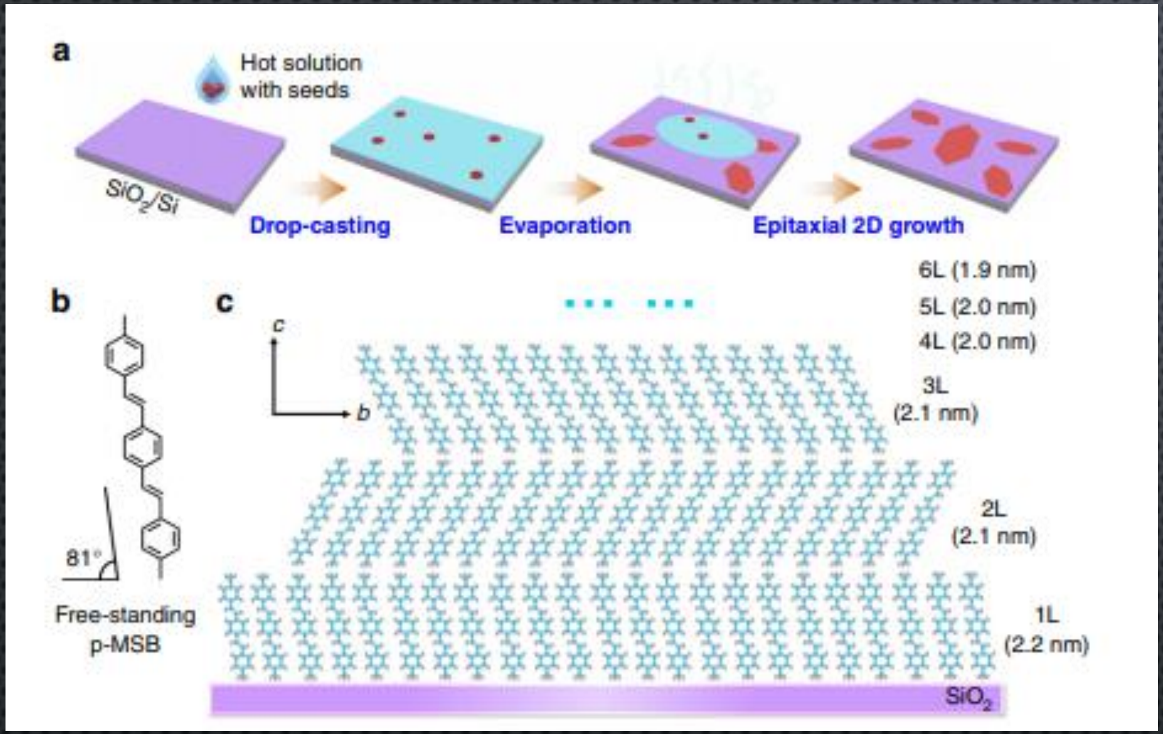


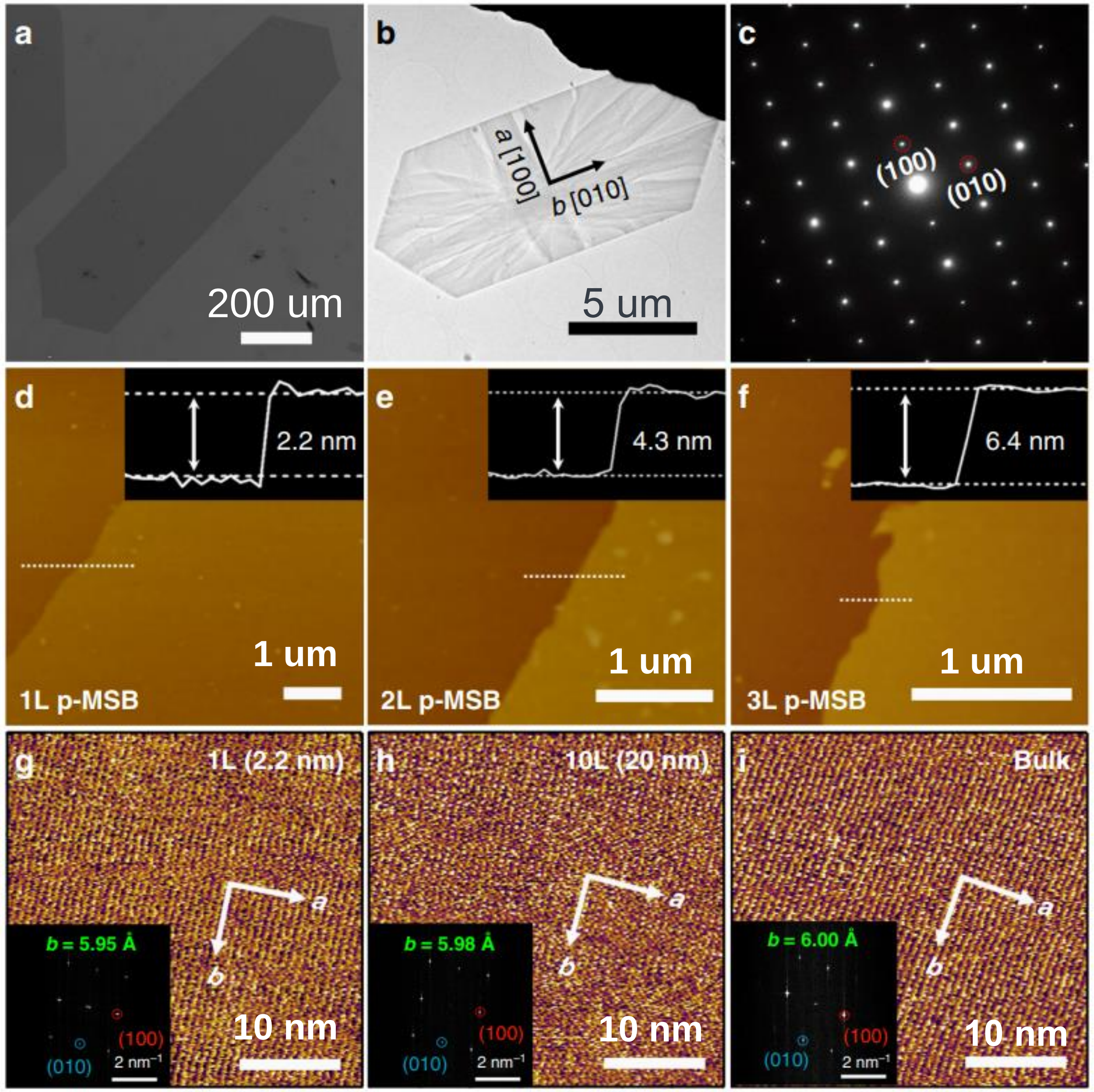


http://www.eng.utah.edu/~lzang/images/Lecture_10_AFM.pdf

http://www.freesbi.ch/en/illustration/figures

High-resolution AFM measurement of 2D materials

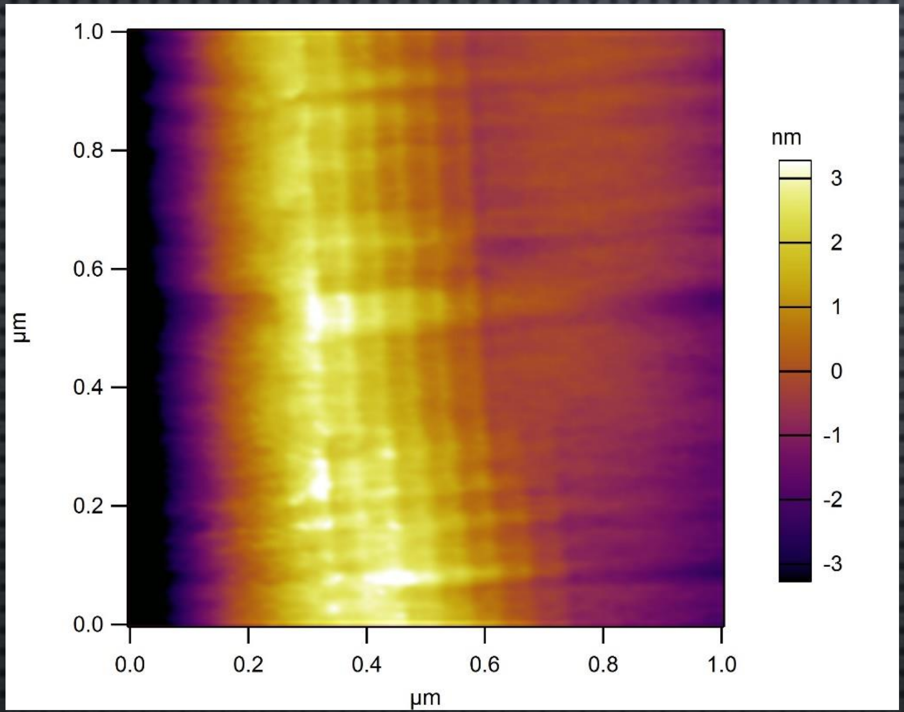


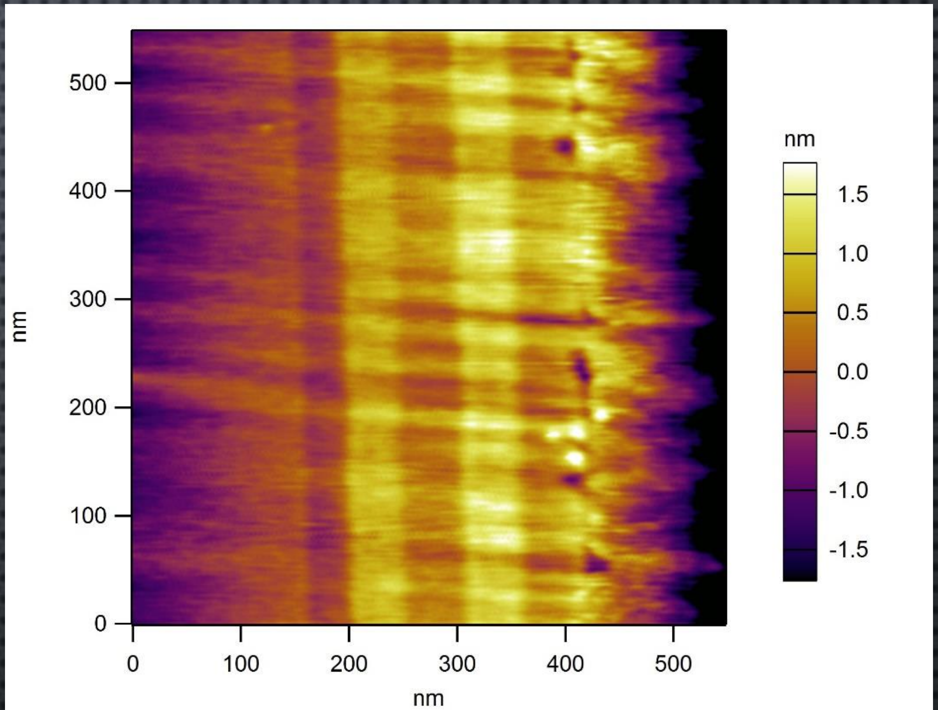


- 2-D p-MSB crystals
- High-resolution AFM measurement was performed under ambient conditions
- Thickness
- Crystallographic structures

Nat. Comm. 2019, **10**, 756

AFM of TEM lamella sample ZnS/GaP multi-layer



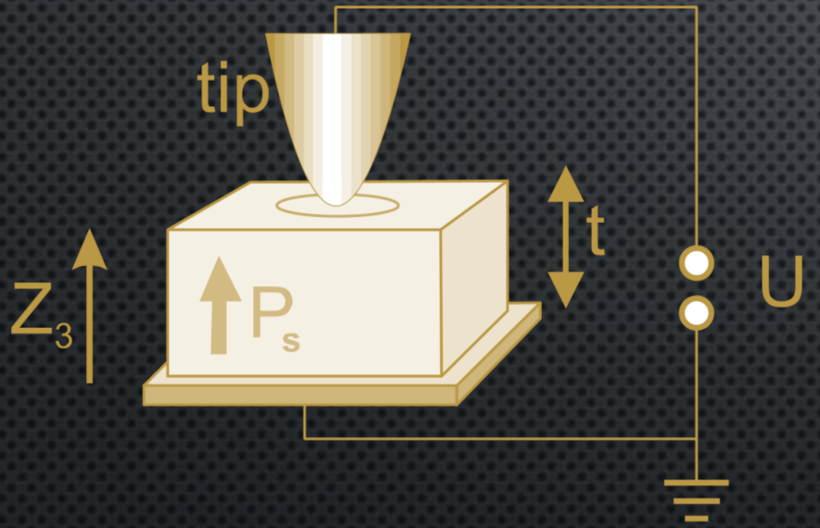


The Journal of Physical Chemistry C 2019, 123, 3336

TYPICAL VARIANTS OF AFM

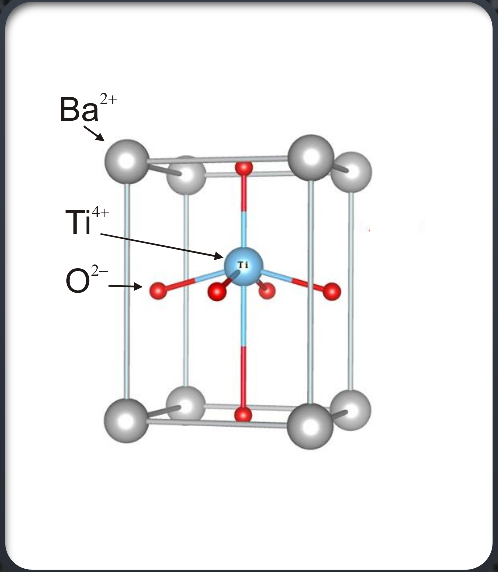
- Piezoresponse force microscopy (PFM)
- Conductive atomic force microscopy (CAFM)
- Electrostatic force microscopy (EFM)
- Kelvin probe force microscopy (KPFM)
- Magnetic force microscopy (MFM)

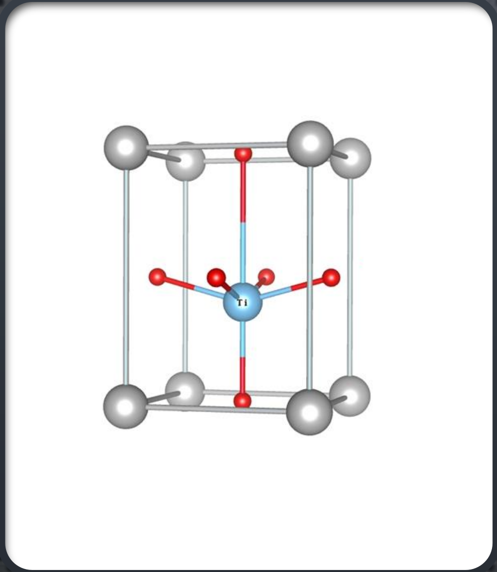
PIEZORESPONSE FORCE MICROSCOPY (PFM)

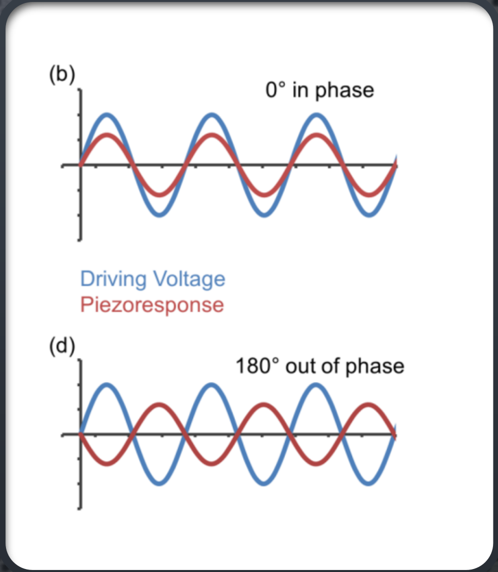


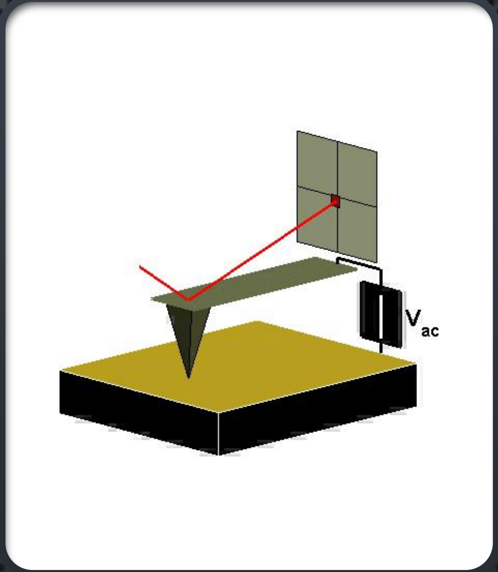
- Top electrode: conductive AFM tip
- Local deformation under the tip
- Inhomogeneous field
- Displacement can be measured

PFM MEASUREMENTS



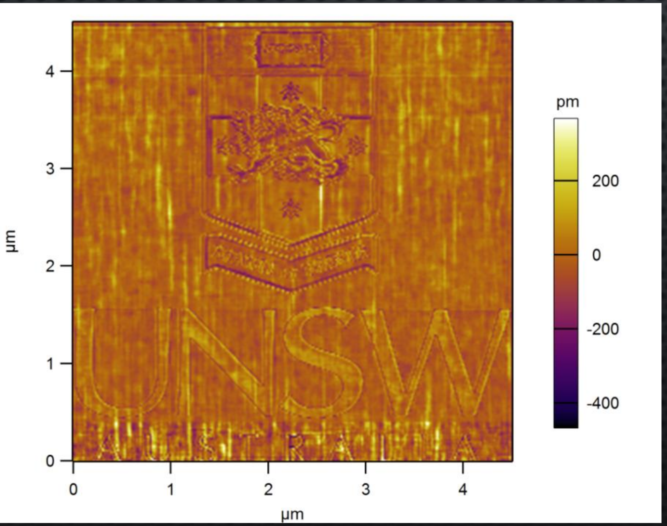


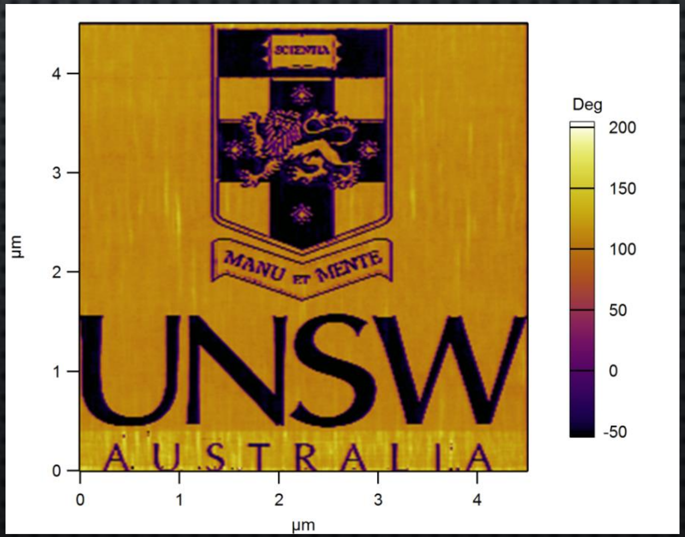




https://afm.oxinst.com/

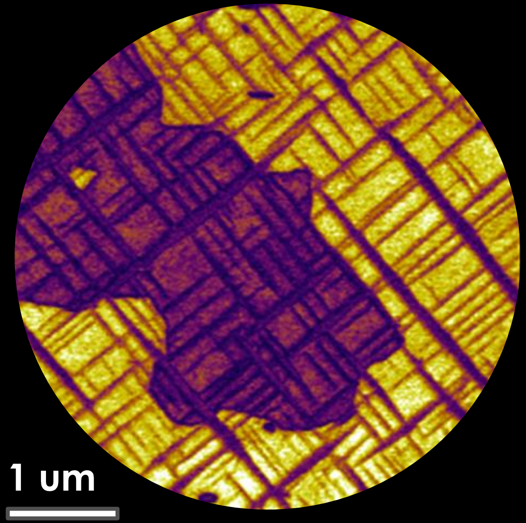
Amplitude



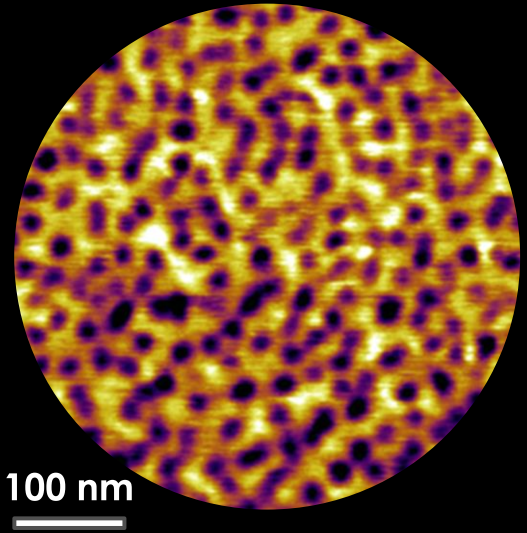


Phase

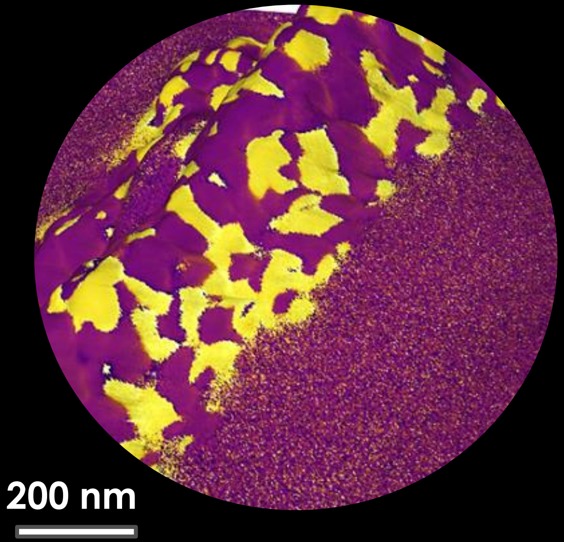
APPLICATIONS



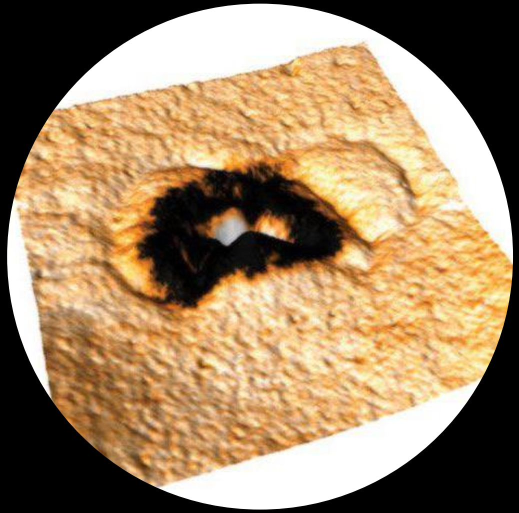
PFM Amplitude
PTO c/a domains



PFM Amplitude
nanoscale bubble domains

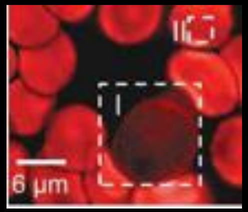


Topography +PFM phase
BFO nanofiber[1]



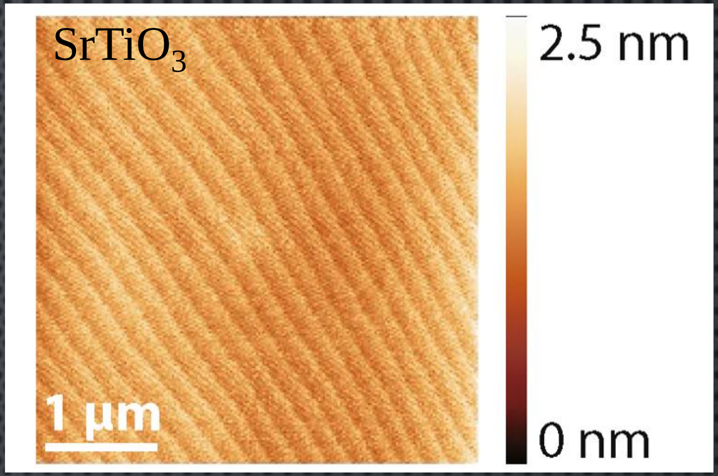
Scan size 2 μm

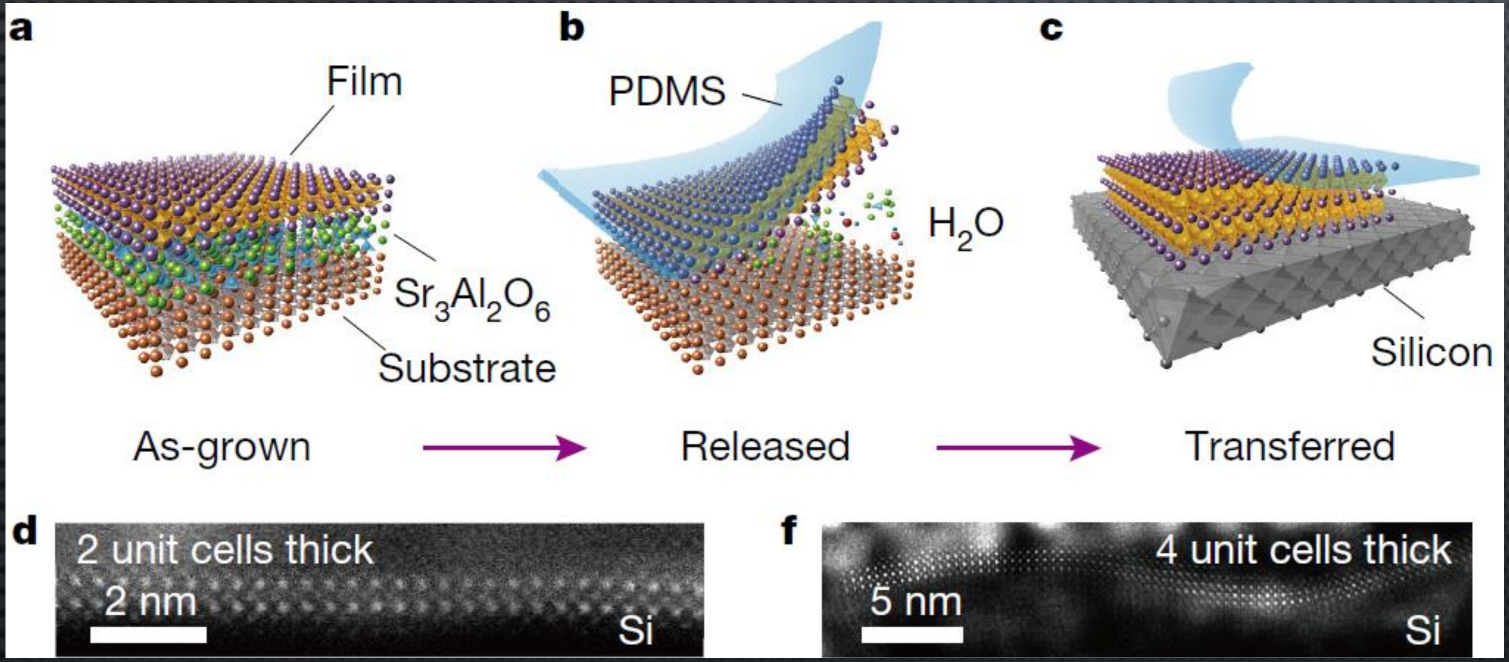
Topography +PFM phase
Blood cell[2]



[1] data from Shuhong Xie (Xiangtan Uni) et.al, Asylum research gallery
[2] data from B. Rodriguez and S. Kalinin, ORNL, Asylum research gallery

Freestanding crystalline oxide perovskites down to the monolayer limit

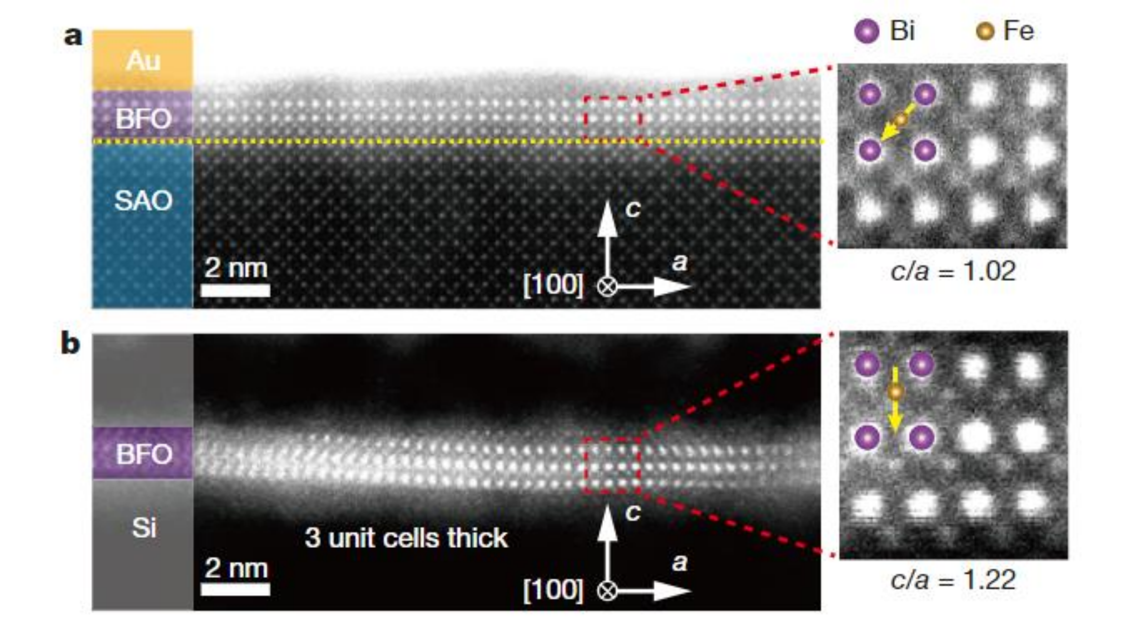


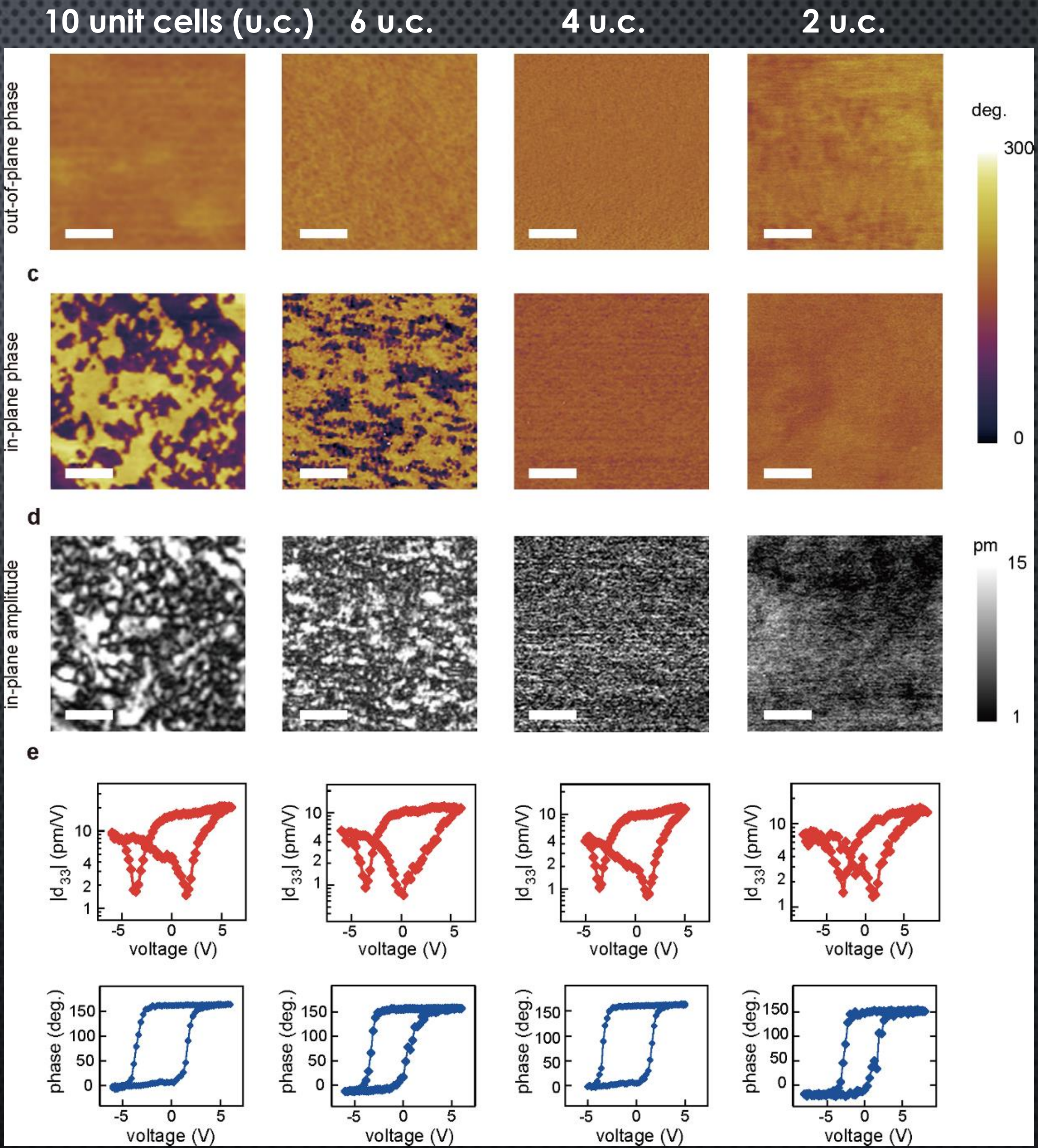


1. Synthesize freestanding $SrTiO_3$ and $BiFeO_3$ ultrathin films by reactive molecular beam epitaxy;
2. Transfer them to diverse substrates, in particular crystalline silicon wafers and holey carbon films.

Fascinating properties of 2D materials make them exciting candidates for next-generation technology in energy, quantum computing, and other applications.

Nature, **2019, 570**, 87



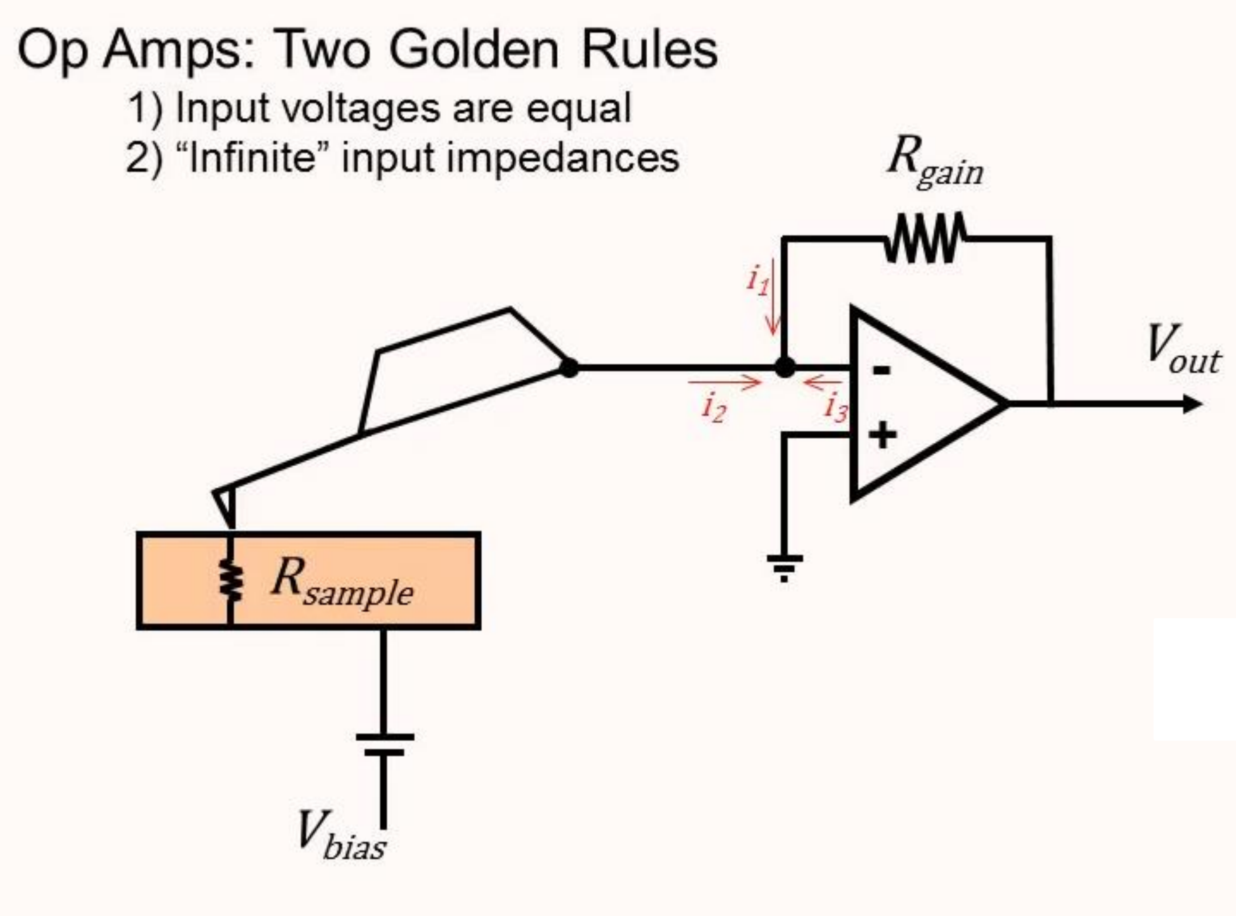


- Freestanding $BiFeO_3$ films exhibit unexpected and giant tetragonality and polarization when approaching the 2D limit.
- PFM revealed giant polarization in BFO, in layers only 2 unit cells thick
- Absence of a critical thickness for stabilizing the crystalline order in the freestanding ultrathin oxide films.

Nature, **2019, 570**, 87

CONDUCTIVE ATOMIC FORCE MICROSCOPY (CAFM)

Imaging while collecting current



$$\frac{V_{out}}{R_{gain}} = \frac{V_{in}}{R_{sample}}$$

$$V_{out} = R_{gain}\left(\frac{V_{in}}{R_{sample}}\right)$$

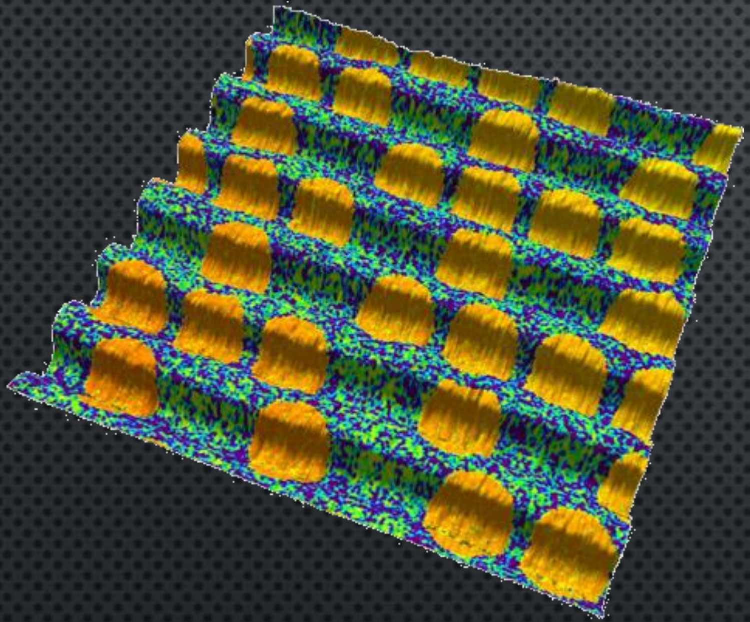
but

$$\frac{V_{in}}{R_{sample}} = I_{in}$$

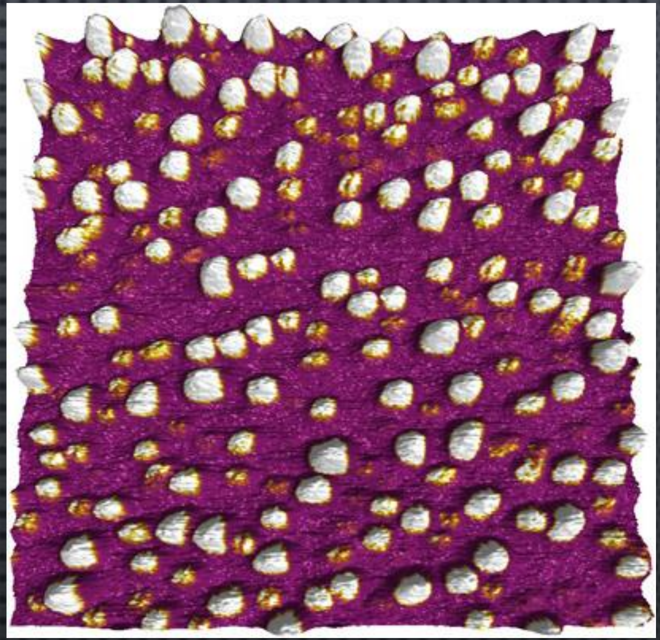
so

$$V_{out} = I_{in} R_{gain}$$

CONDUCTIVE AFM



CAFM of DVD Recording



- **Conductive AFM on Gallium arsenide (GaAs) Quantum Dots**
- The conductivity data (white) is overlaid on rendered topography, 700nm scan.
- **Sample courtesy of T. Jones, The University of Warwick.**

Photo current at zero applied bias
Polymer self assembled nanofibers.

Image courtesy of D. Kamkar and T.-Q. Nguyen, UCSB.

Source: Asylum research gallery

Voltage-dependent current map on vertically aligned carbon nanotubes (CNTs)

Topography | Current map | I-V curves

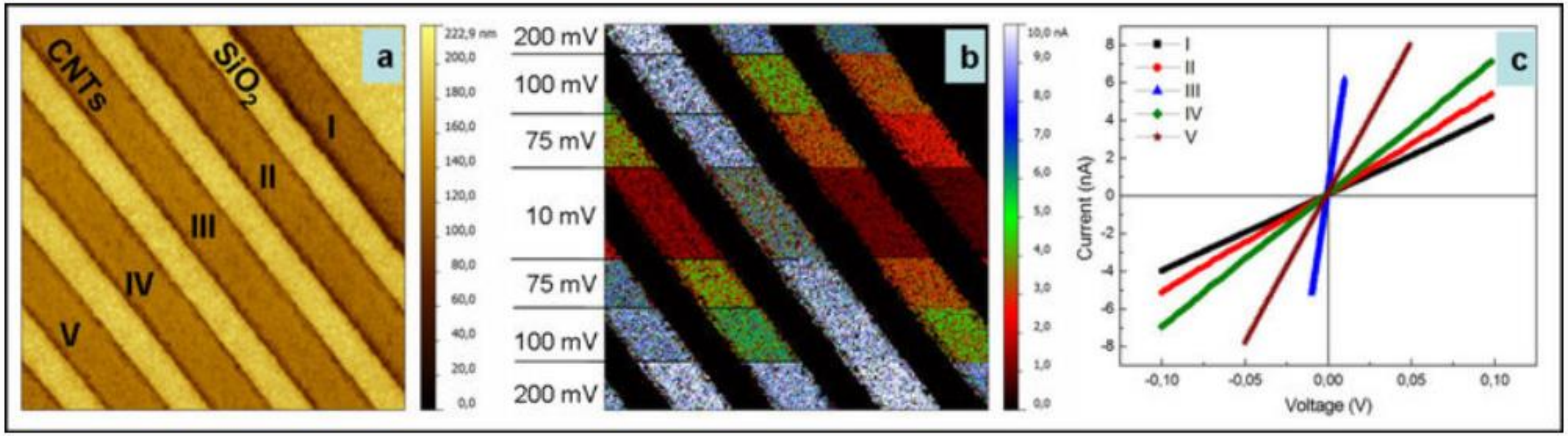


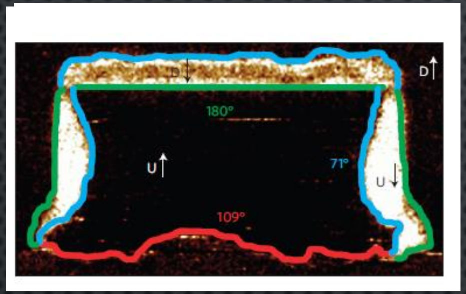
Figure 5

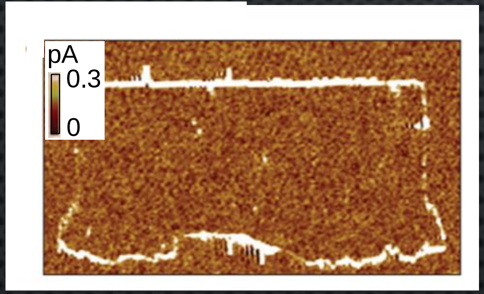
Topography (a) vs. voltage-dependent current map (b); corresponding *I* - *V* characteristics of indicated MWCNT arrays (c).

Nanoscale Research Letters 2013, **8,** 24

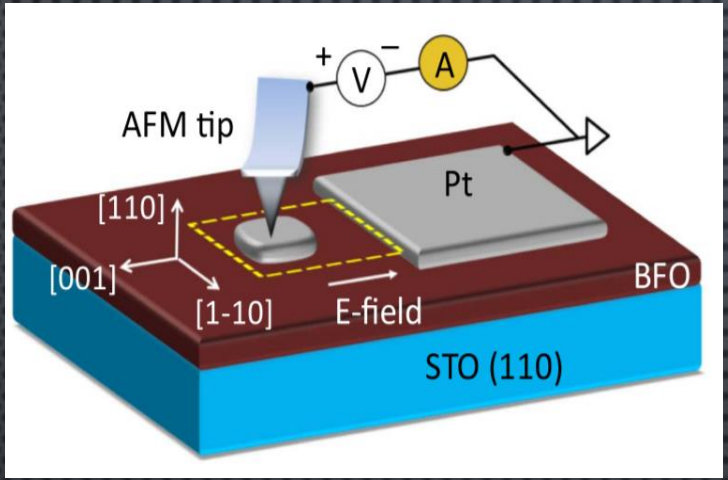
Domain wall conductivity

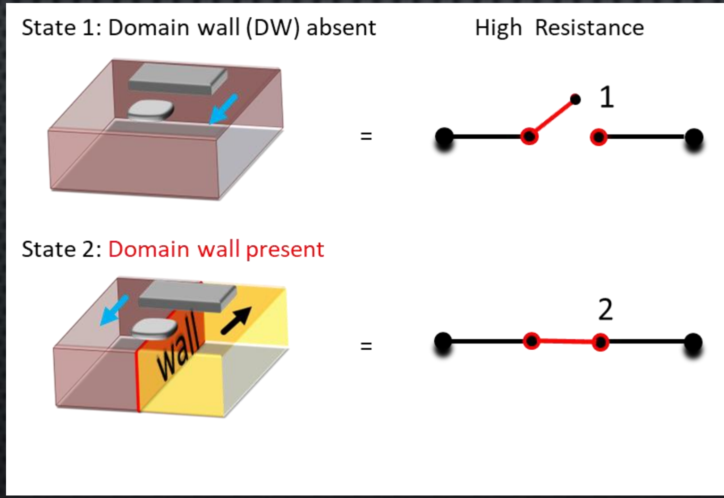
Multiferroic $BiFeO_3$ thin films

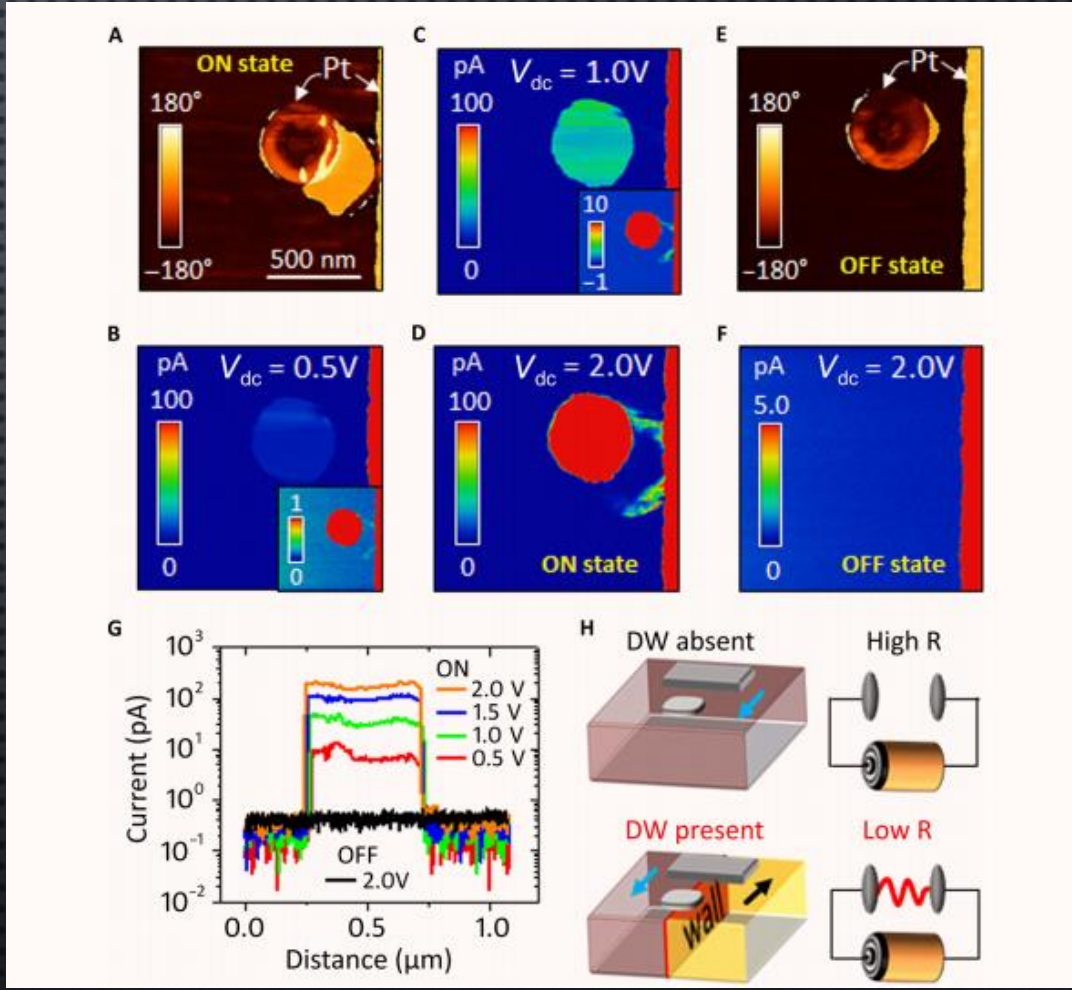




Seidel, *et al. Nat. Mater.* 8, 229-234 (2009)
Lubk, *et al. Phys. Rev. B* 80 104110 (2009)

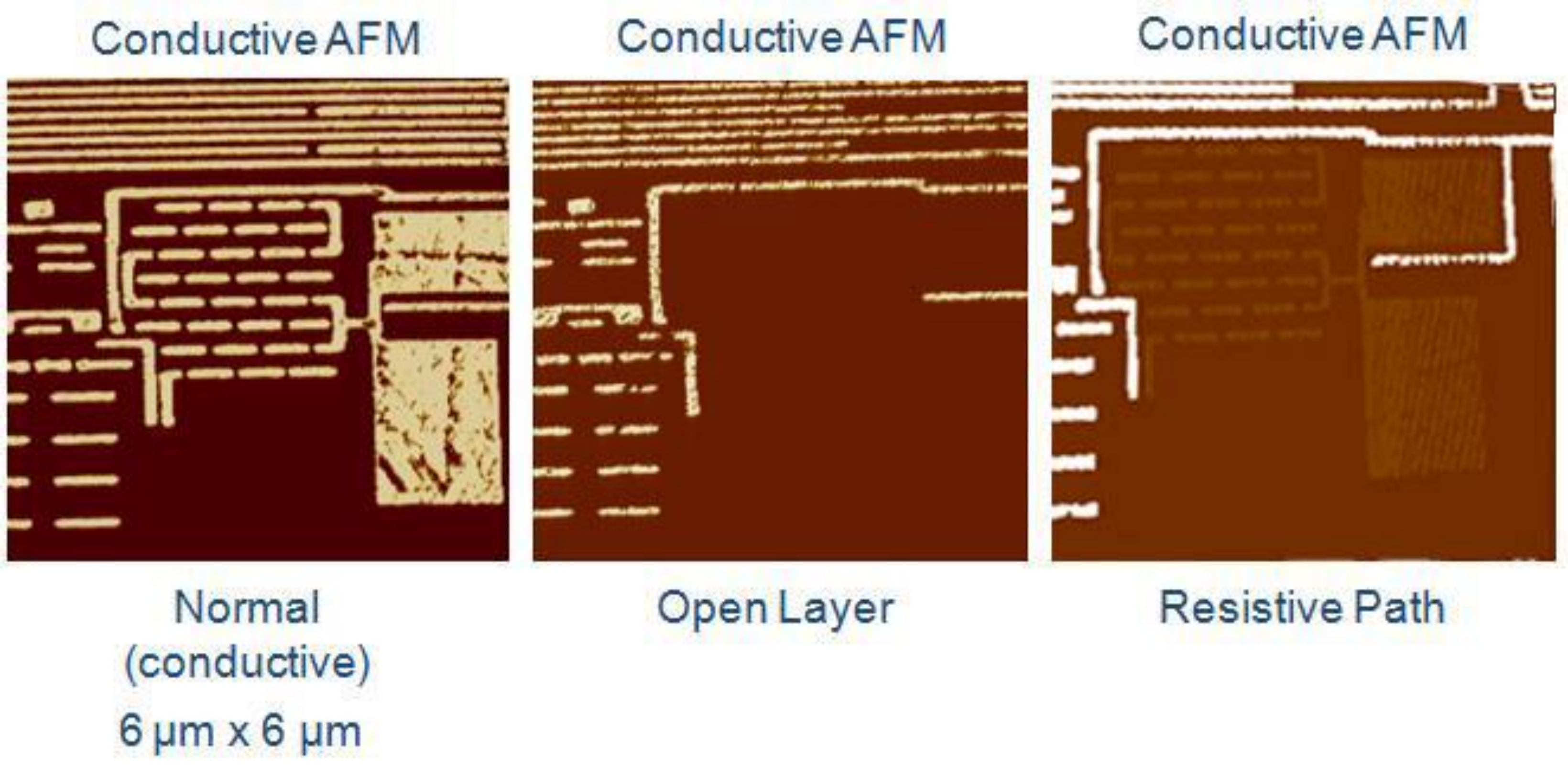






P.Sharma, et al. Sci. Adv. 2017, 3, e1700512

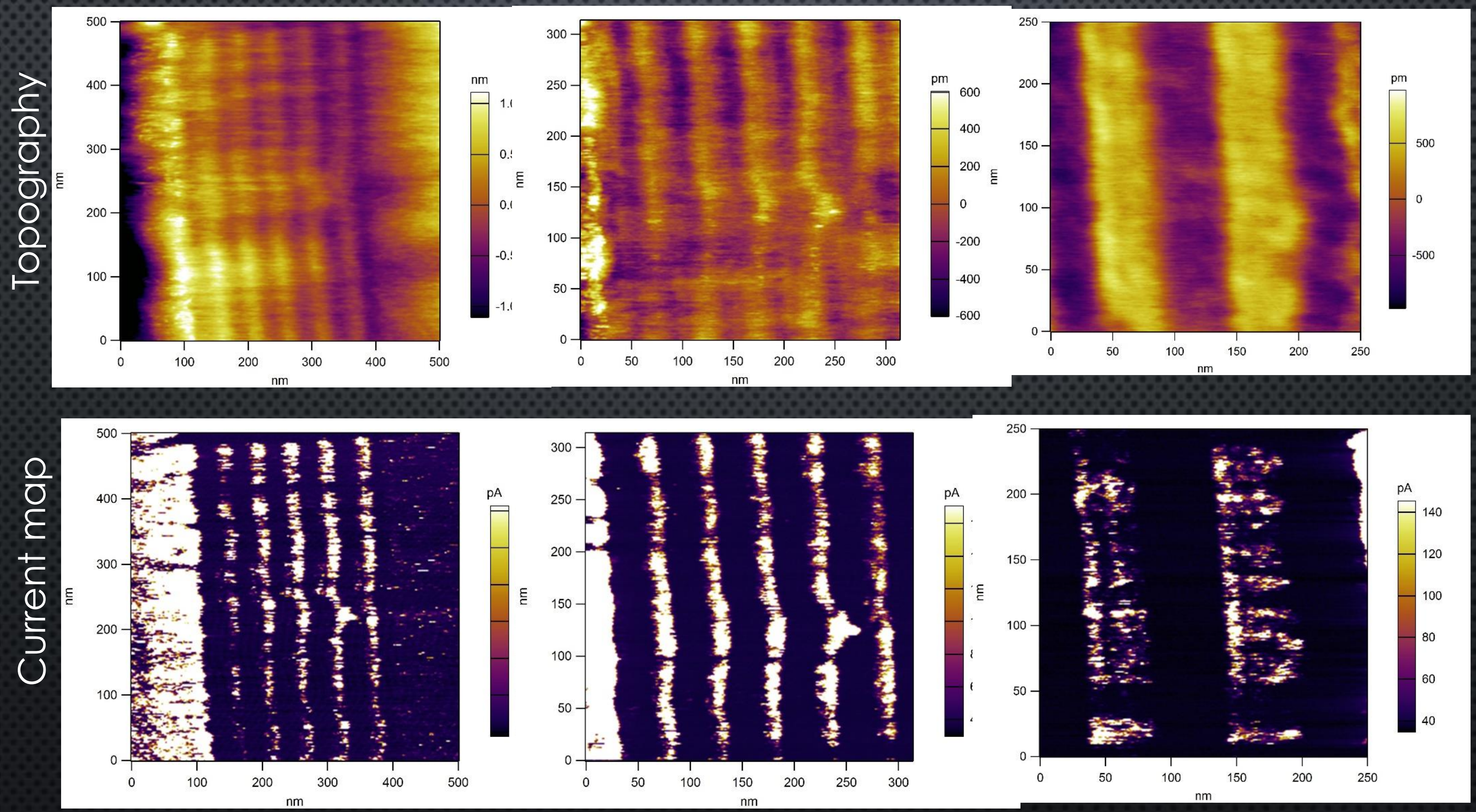
Device Testing



https://www.parksystems.com/index.php/medias/resources/afm-images/electrical-electronics/ic-device

IC Device. Conductive AFM images of IC showing the failure of conducting wires as normal, open, and resistive.

Conductive AFM of TEM lamella sample
Zinc sulfide/ Gallium phosphide (ZnS/GaP) multi-layer



The Journal of Physical Chemistry C 2019, 123, 3336

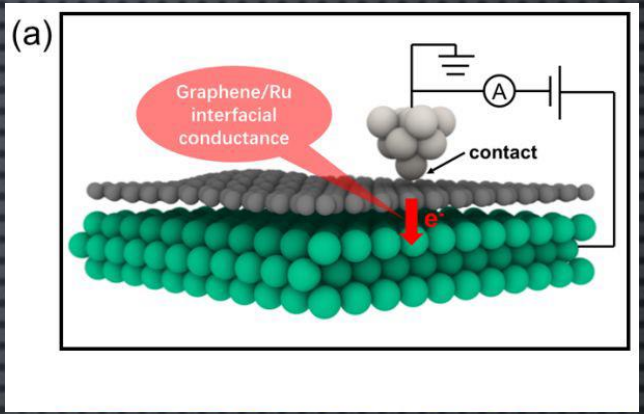
NANO LETTERS

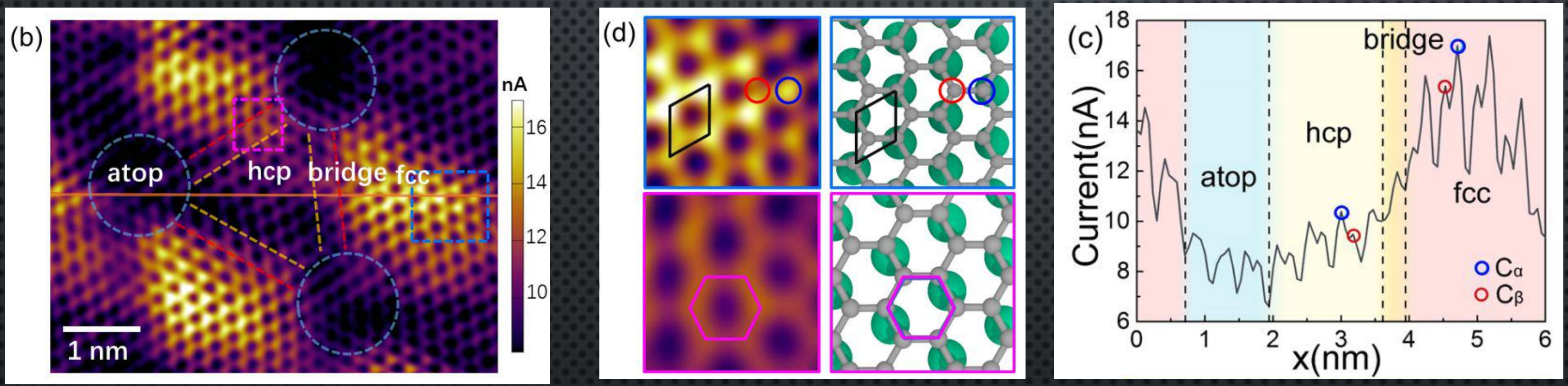
Communication

Modelling atomic-scale electrical contact quality across two-dimensional interfaces

Aisheng Song, Ruoyu Shi, Hongliang Lu, Lei Gao, Qunyang Li, Hui Guo, Yanmin Liu, Jie Zhang, Yuan Ma, Xin Tang, Shixuan Du, Xin Li, Xiao Liu, Yuanzhong Hu, Hongjun Gao, Jianbin Luo, and Tianbao Ma

Nano Lett., **Just Accepted Manuscript** • DOI: 10.1021/acs.nanolett.9b00695 • Publication Date (Web): 15 May 2019





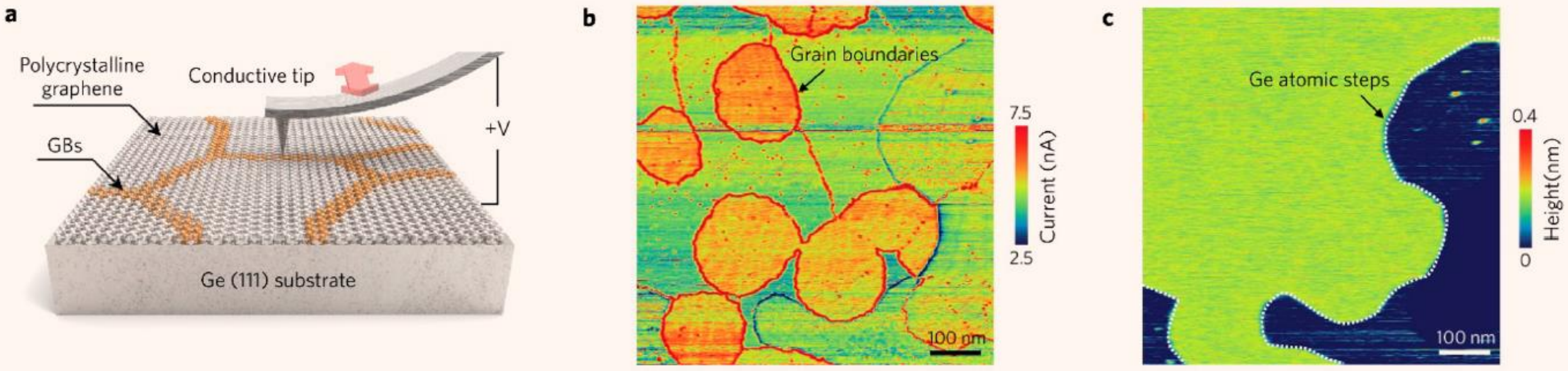
Nano Lett. 2019, 19, 3654

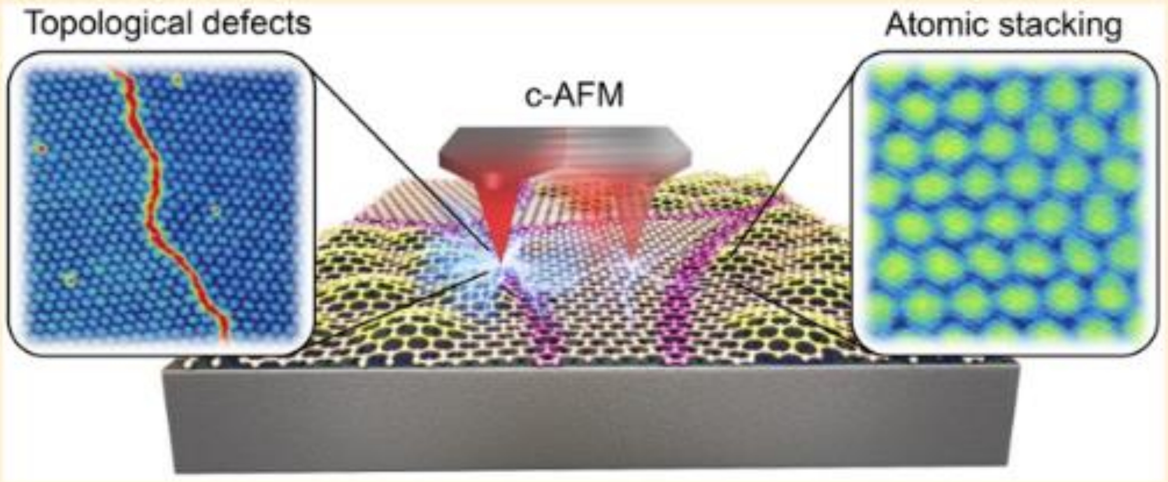
- Graphene/Ruthenium
- CAFM in air. Limited influence from humidity and environment
- Images in (d) correspond to blue and pink boxes in (b) with scan size 1 nm.
- The atomic-scale AFM images allowed them to directly relate local contact quality to interfacial atomistic structure.
- The new model described the effect of varying the relative orientation angle of graphene.
- Applying this model to other interfaces with 2D materials should help establish design guidelines for tuning interfacial electrical contact on the atomic scale.

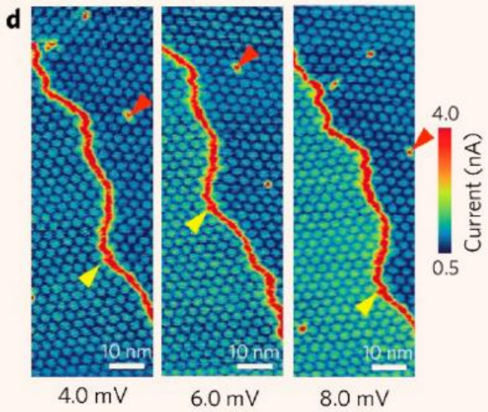
NANO LETTERS
Letter
Cite This: *Nano Lett.* XXXX, XXX, XXX−XXX
pubs.acs.org/NanoLett

Tuning Local Electrical Conductivity via Fine Atomic Scale Structures of Two-Dimensional Interfaces

Shuai Zhang,[†,‡] Lei Gao,[‡,§] Aisheng Song,[‡] Xiaohu Zheng,[∥] Quanzhou Yao,[†] Tianbao Ma,[*,‡] Zengfeng Di,[∥] Xi-Qiao Feng,[†,‡] and Qunyang Li[*,†,‡]



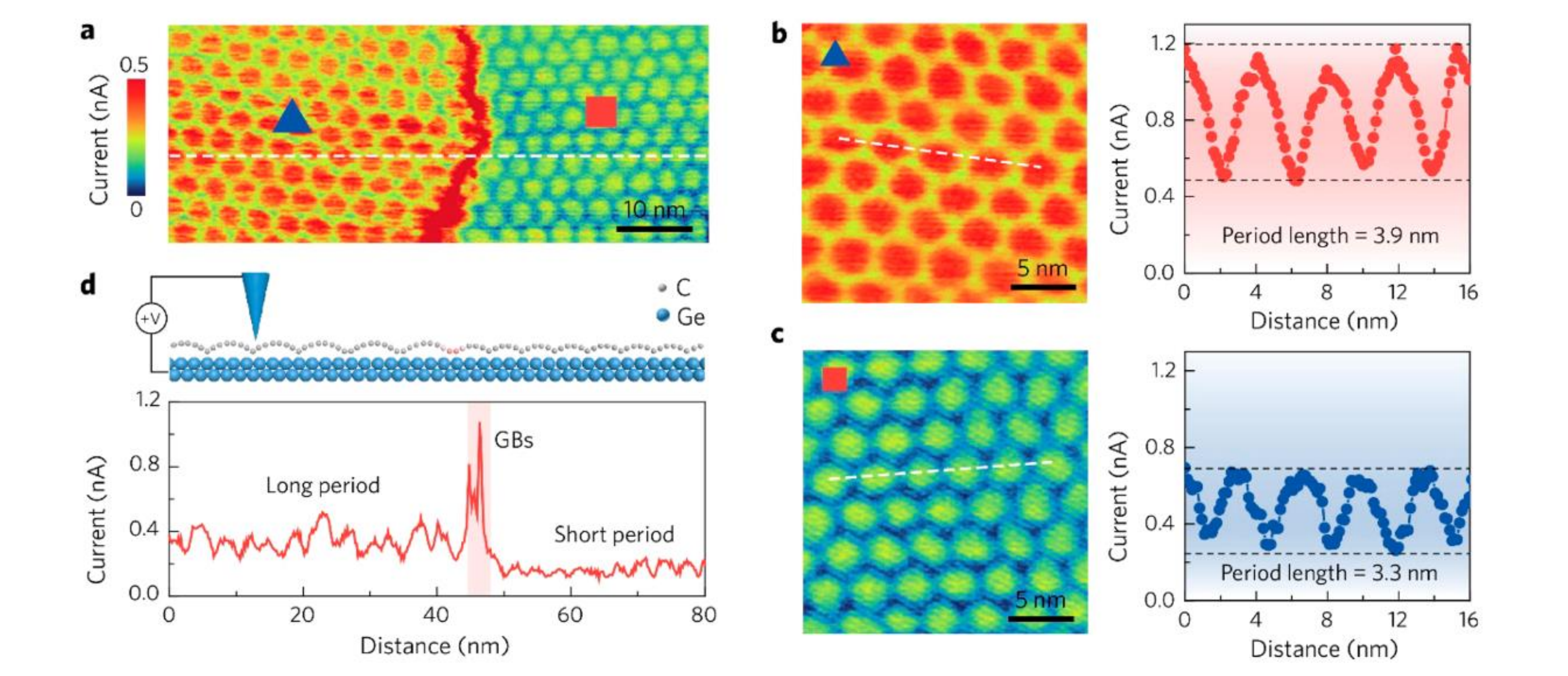




- Materials: graphene /Ge(111)
- Conductive probe
- Ambient conditions

  (20−25°C, relative humidity 20−30%)
- Using lattice-resolved conductivity mapping and first-principles calculations
- The electronic charge transfer has been demonstrated
- Conductive grain boundary
- Electrical conductivity can be fine-tuned by the topological defects of 2D materials and the atomic stacking with respect to the substrate.

Nano Lett. 2018, 18, 6030

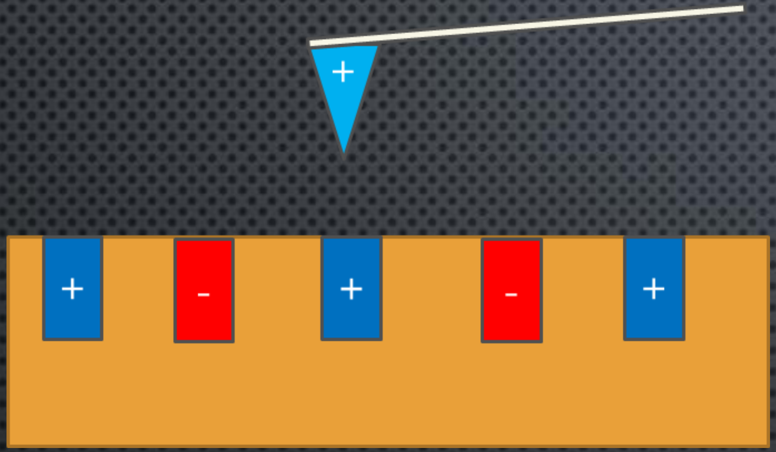


- A typical current image contained two distinct regions, long-period and short-period moiré patterns, which which shows a sharp contrast in conductivity.
- The current measurement in c-AFM directly confirms that the enhancement at the GB and the superlattice superlattice level modulation in current are originated from the variation of local contact conductivity.

Nano Lett. 2018, 18, 6030

ELECTROSTATIC FORCE MICROSCOPY (EFM)

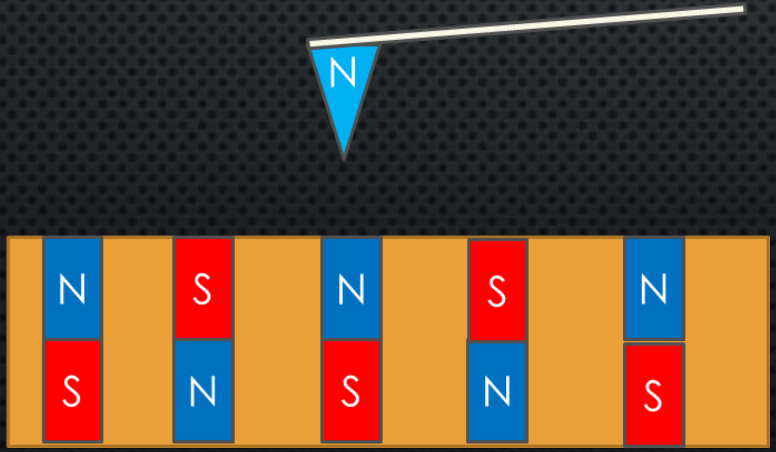
MAGNETIC FORCE MICROSCOPY (MFM)



Electrostatic force microscopy (EFM) is a type of dynamic **non-contact** atomic force microscopy where the electrostatic force is probed.

("Dynamic" here means that the cantilever is **oscillating** and does not make contact with the sample).

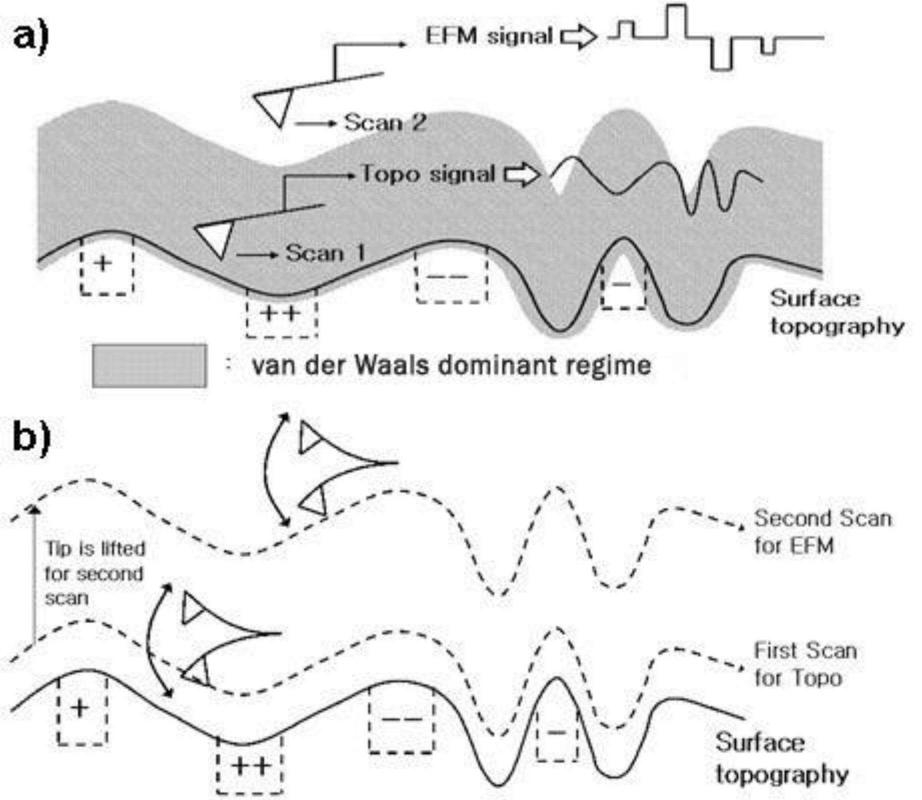
This force arises due to the attraction or repulsion of separated charges. It is a long-range force and can be detected 100 nm or more from the sample.



Magnetic force microscopy (MFM) is a variety of atomic force microscopy, in which a sharp magnetized tip scans a magnetic sample; the tip-sample magnetic interactions are detected and used to reconstruct the magnetic structure of the sample surface

-- Wikipedia

Measurement principles



https://www.parksystems.com/images/spmmodes/dielectric/Electrostatic-Force-Microscopy-(EFM).pdf?ver=1.2

- The first scan: scanning the tip near the surface as it is done in NC-AFM (the van der Waals forces are dominant)

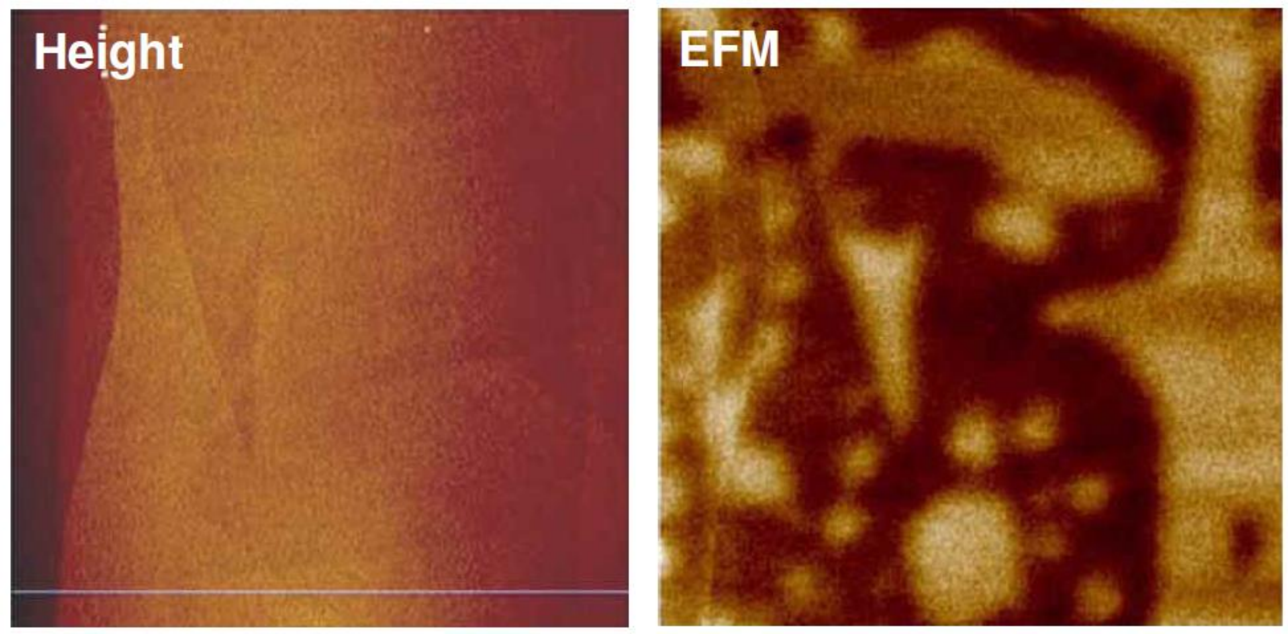
- The second scan: increases the tip-sample distance where electrostatic/magnetic forces are dominant.

- The tip is then biased and move parallel to the topography line obtained from the first scan (constant tip-sample distance.).

- Here the only source of the signal change will be the change of the electrostatic/magnetic force.

EFM

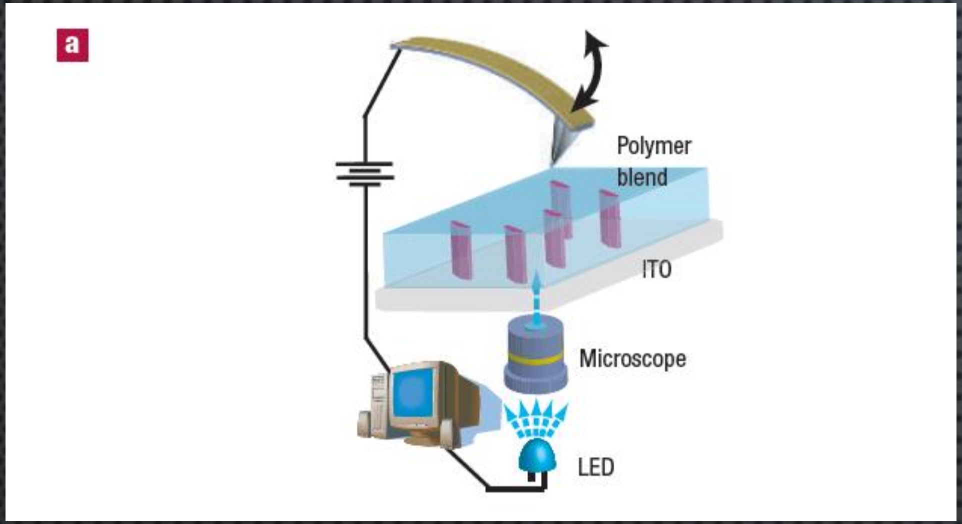
Electrostatic Force Microscopy on Oriented Graphite Surfaces:
Where Insulating and Conducting Behaviors Coexist

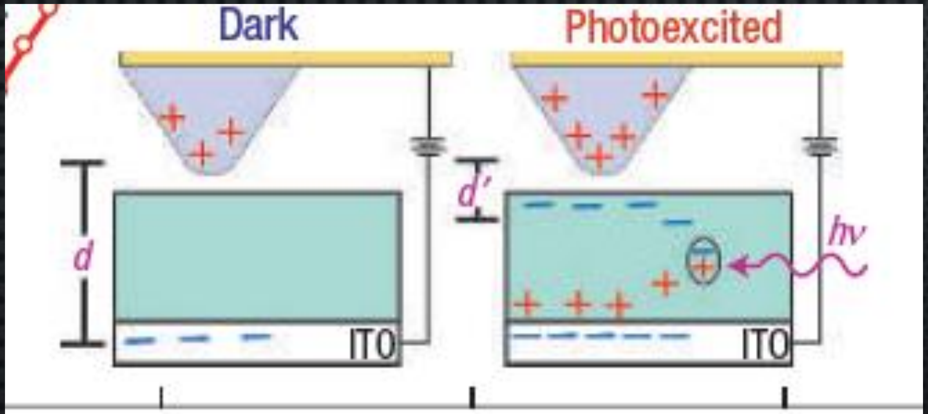


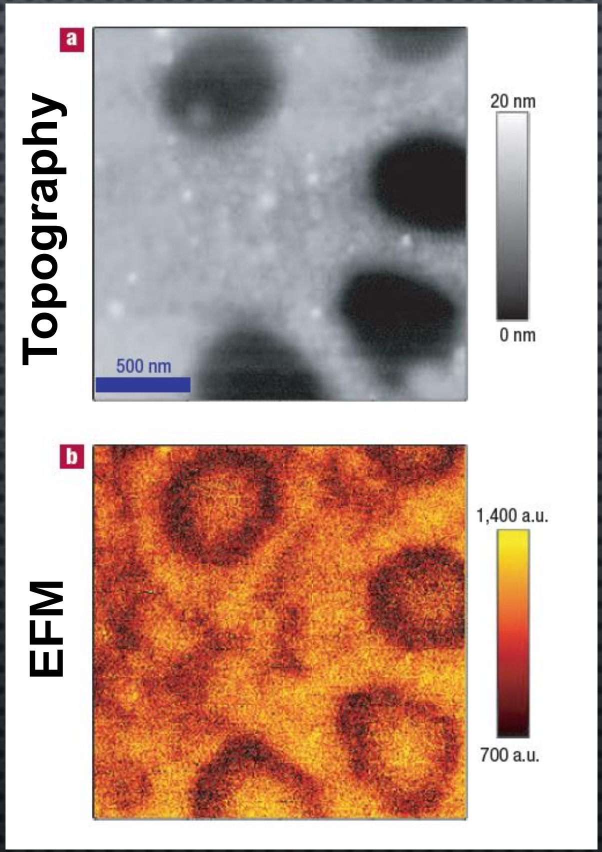
- A domain-like signal feature from EFM
- 3 V voltage on the tip and 100 nm lift-up distance.
- The scans show bright (less conducting or insulating ike)

Phys. Rev. Lett. 2006, **97**, 076805

Time-resolved electrostatic force microscopy of polymer solar cells







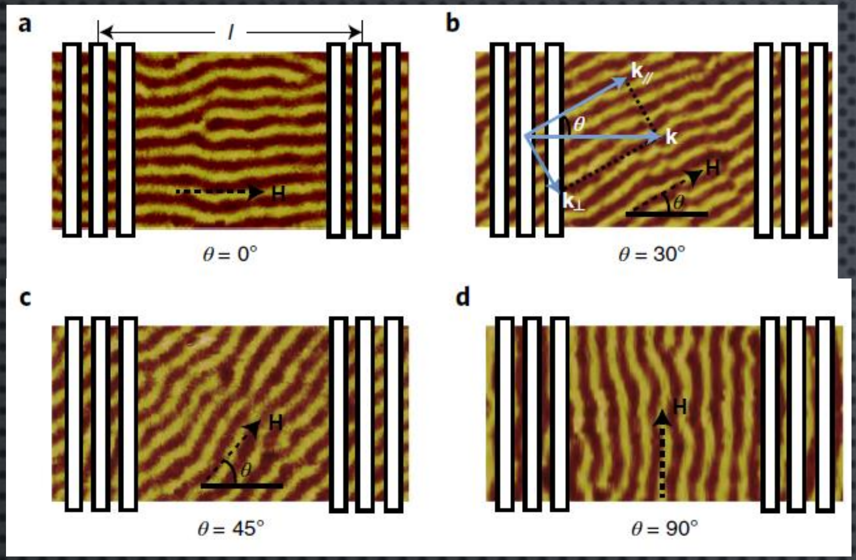
The dark rings indicate regions of slower charging

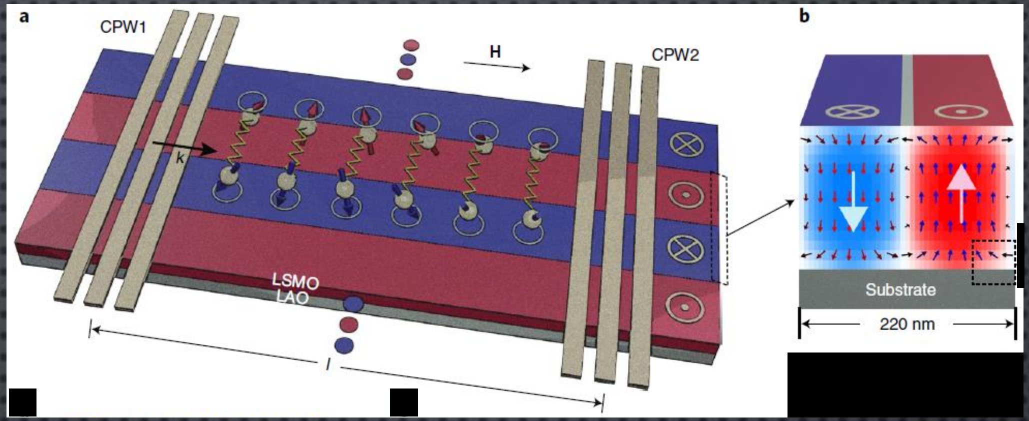
- Material: P8BT/PFB polymer blend
- Low-cost photovoltaic device
- Introduce time-resolved electrostatic force microscopy (EFM) as a means to measure photoexcited charge in polymer films
- The data show that the domain centres account for the majority of the photoinduced charge collected in polyfluorene blend devices

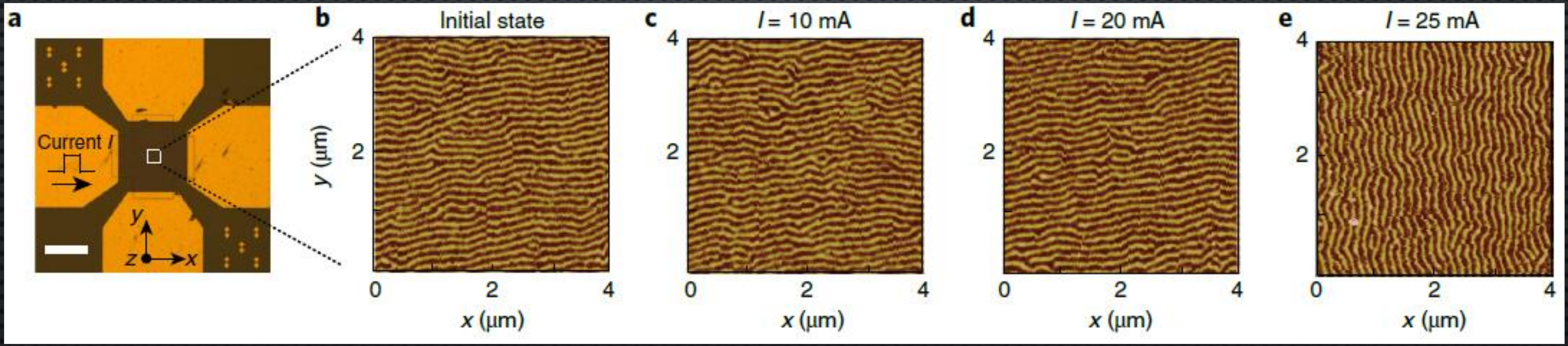
Nature Materials, 2006, **5**, 735

MFM on

Sample is $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) film with 100-nm domains





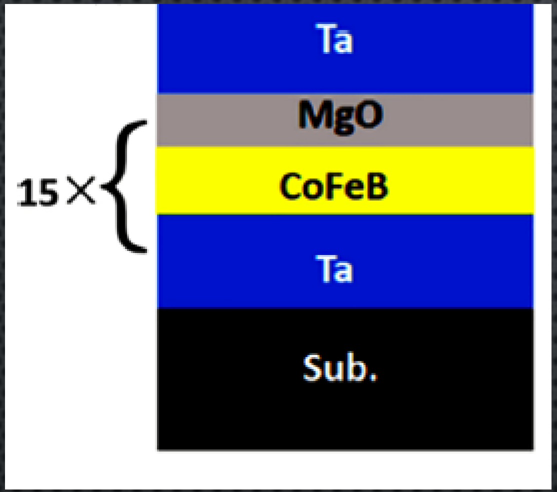


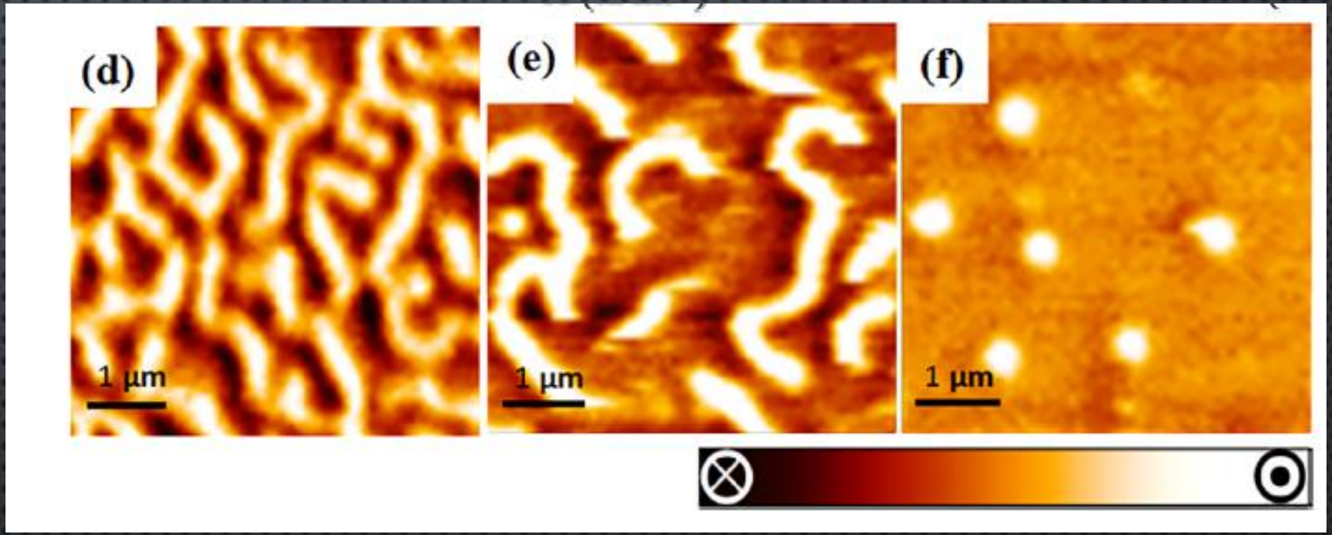
-The domain stripes remained unchanged up to 20 mA, but were reoriented with an applied cur-rent of 25 mA.

-The ability to control spin waves in ordered magnetic materials could enable new types of fast, low-power memory and logic devices.

Nature Nanotechnology, 2019, 14, 691

Skyrmion in Ta/CoFeB/MgO Multilayers

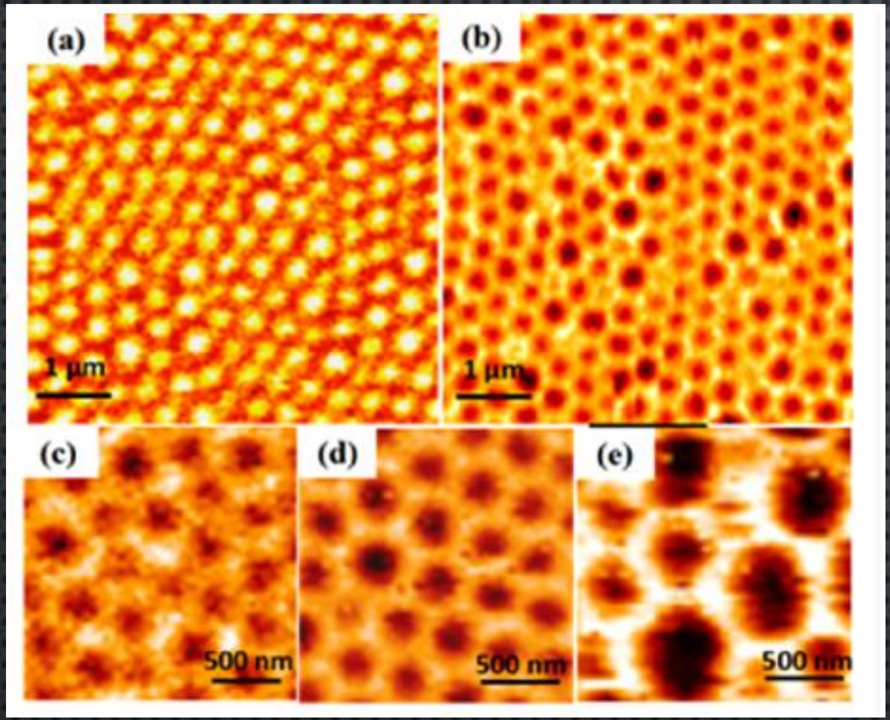


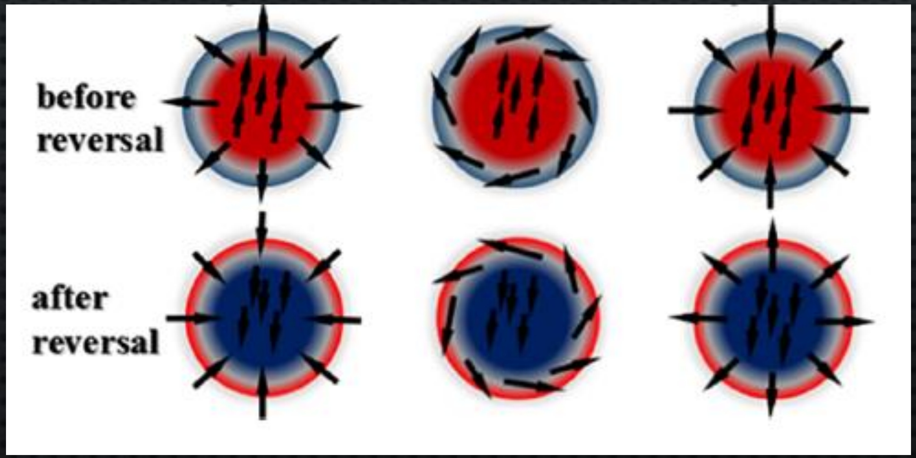


MFM under an out-of-plane magnetic field of 0 mT, 18 mT, 24 mT

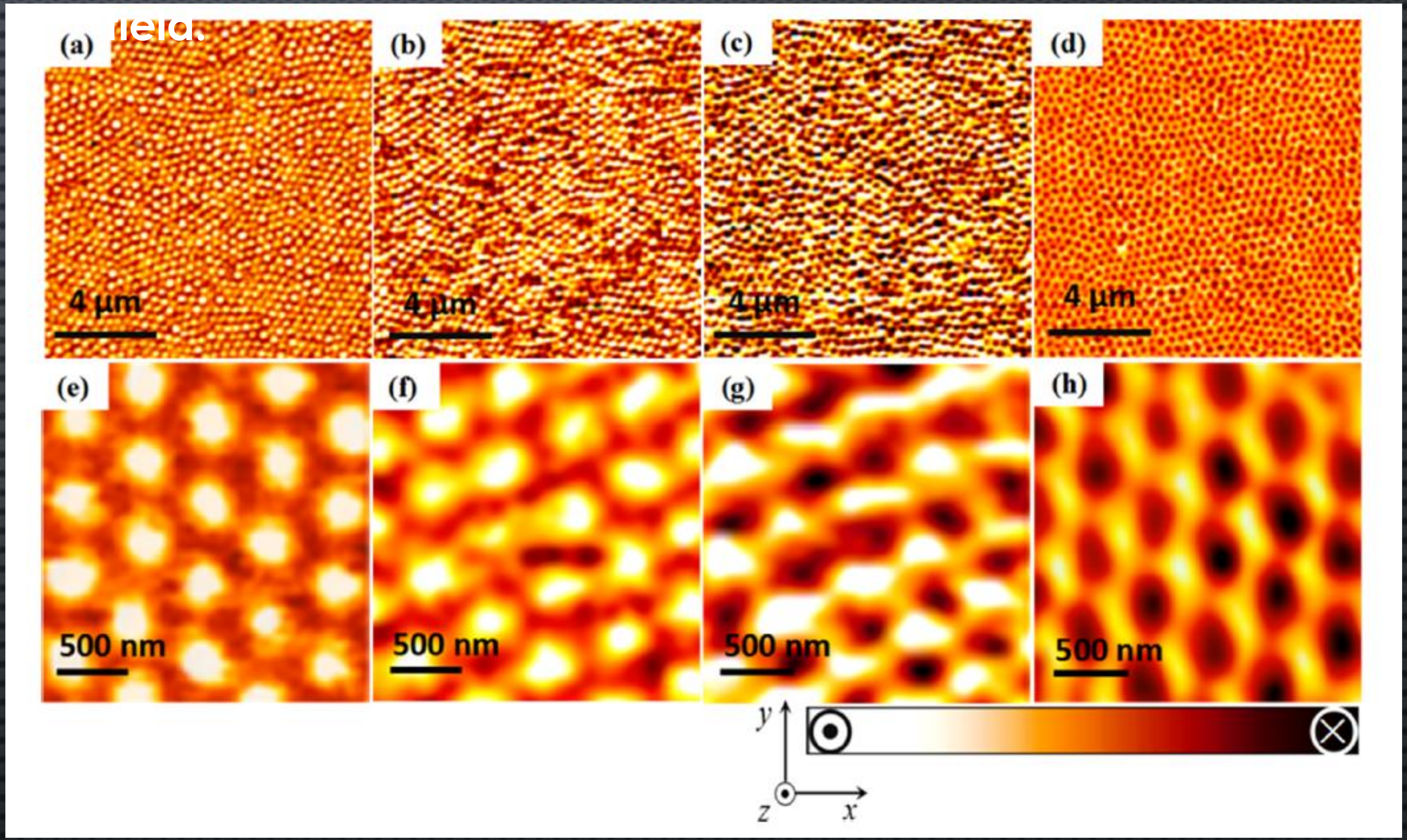
ACS Appl. Mater. Interfaces,2018, 10, 36556

Reversal of the skyrmion lattice under an out-of-plane field.





Reversal of the skyrmion lattice an in-plane titled magnetic field.



MFM images of the skyrmion lattice in a titled in-plane field of (a, e) 0 mT, (b, f) 160 mT, (c, g) 190 mT and (d,h) 0 mT.

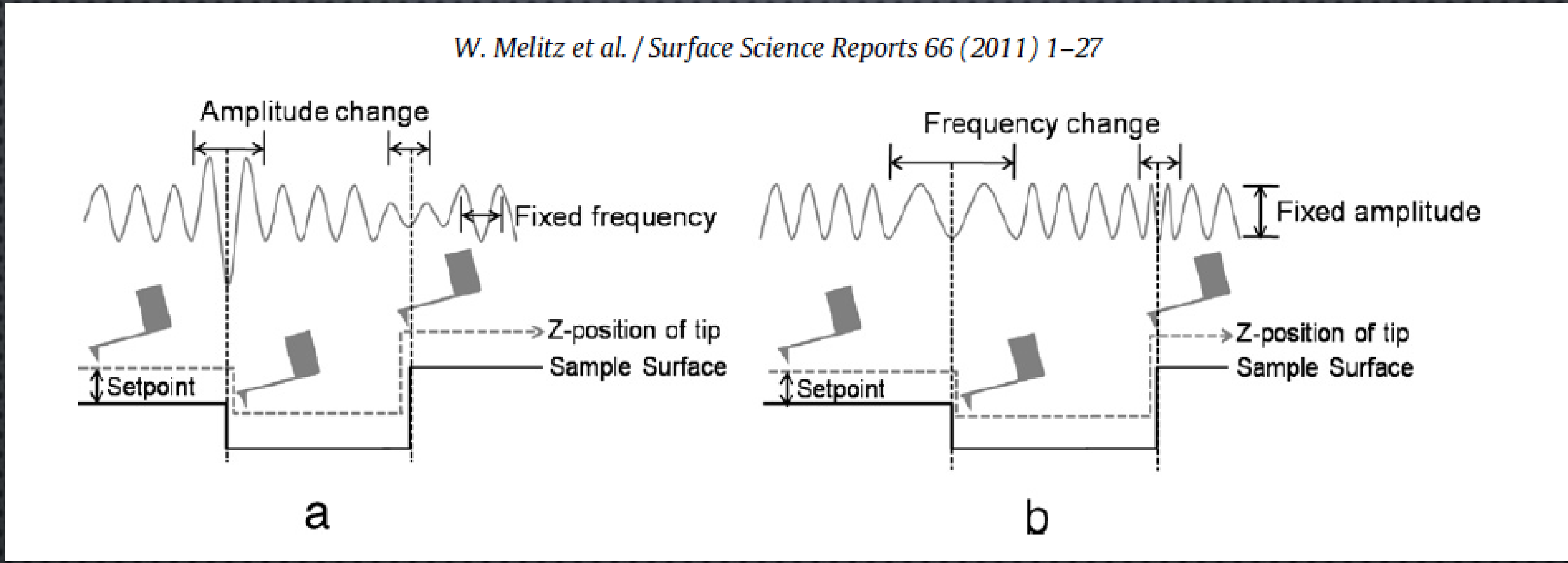
ACS Appl. Mater. Interfaces,2018, 10, 36556

KELVIN PROBE FORCE MICROSCOPY (KPFM)

- Scanning Kelvin probe microscopy (SKPM) is a technique that attempts to ascertain the potential difference between the probe tip and the sample.

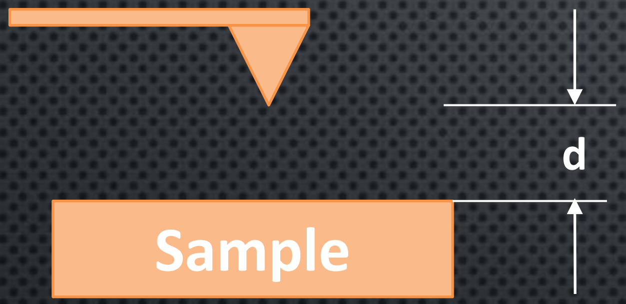
  - **Trapped Charge**
  - **Spontaneous Polarization**
  - **Work function variation**
  - **Potential difference**

KELVIN PROBE FORCE MICROSCOPY



- AC bias sent to tip (matched to fundamental lever frequency)
- Difference in potential causes cantilever oscillations
- Feedback sends DC bias to cantilever, nulling oscillations
- Quantitative measurements of the surface's potential
- Trapped charge, surface polarization, work function, or applied voltage can be measured

Calculate sample work function using KPFM



Changes with d, $C = \varepsilon A/d$

↓

$C = Q/\Delta V$

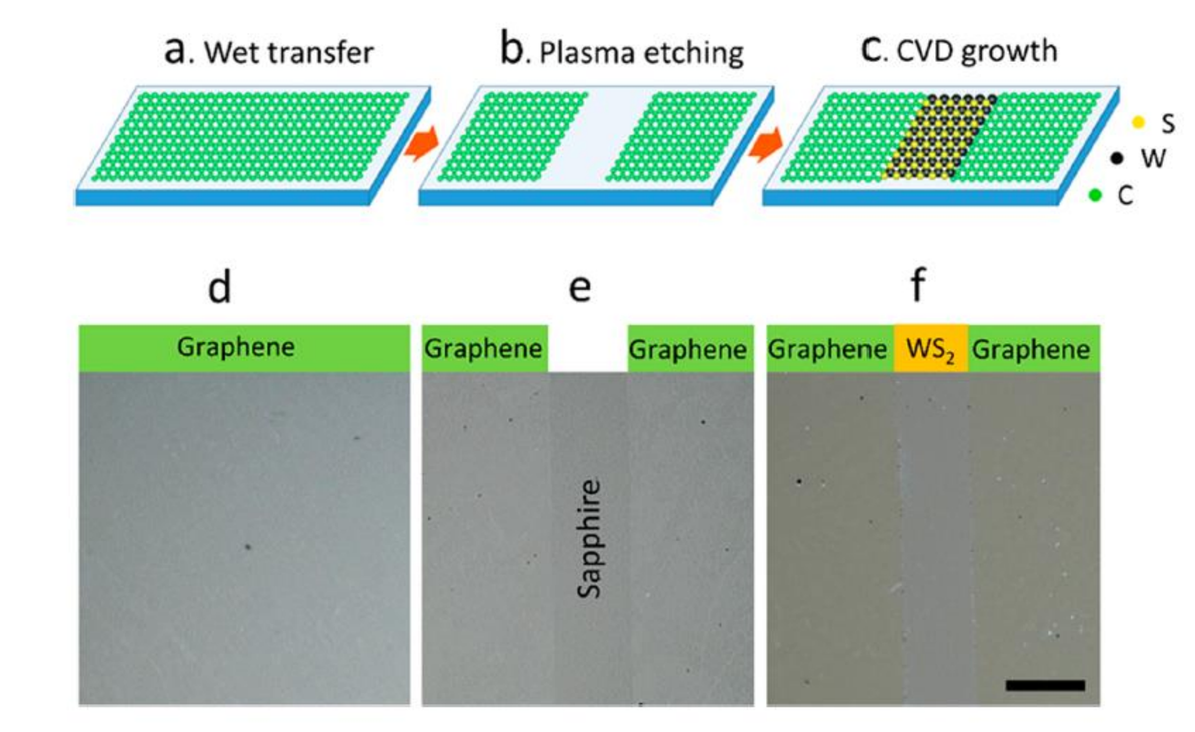
↑

known

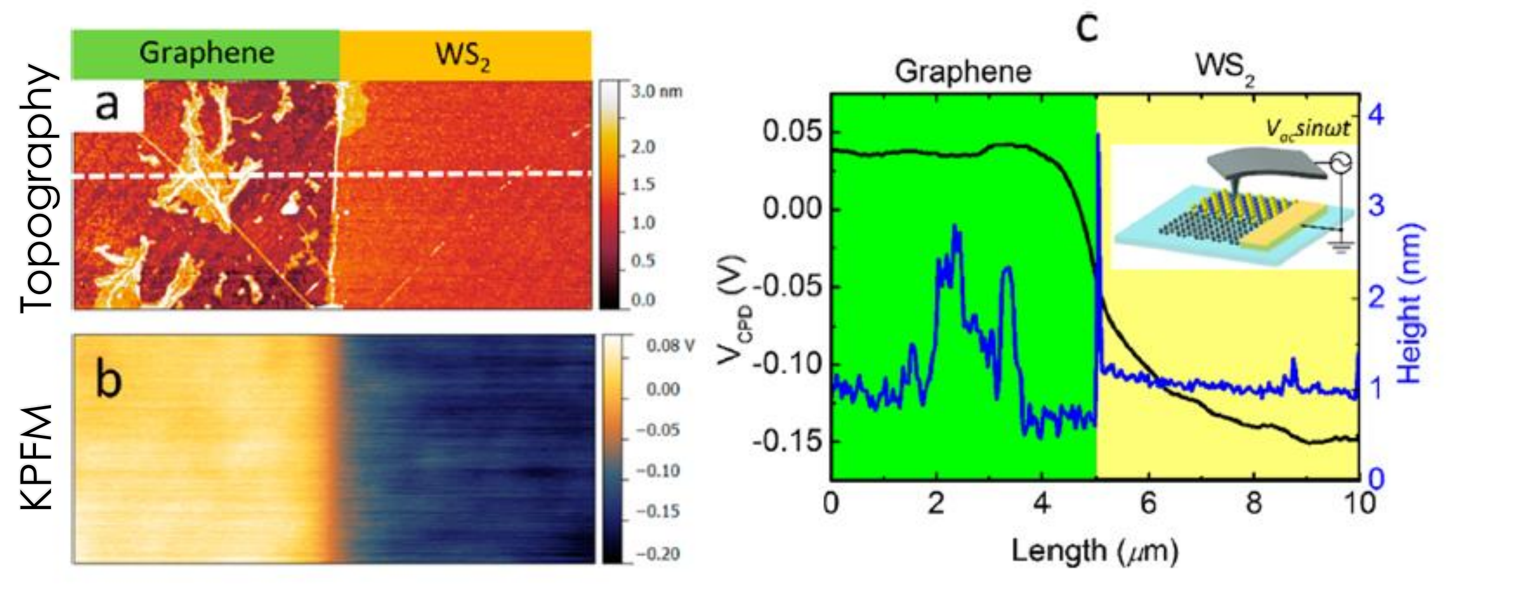
$\Delta V = V_{CPD}$ ➔ Δ work function $= \Phi_{tip} - \Phi_{sample}$

CPD: contact potential difference

Graphene–WS_2 2-dimensional heterojunctions



- AFM and KPFM were employed to investigate the morphology and the correlated surface potential of the heterojunction.



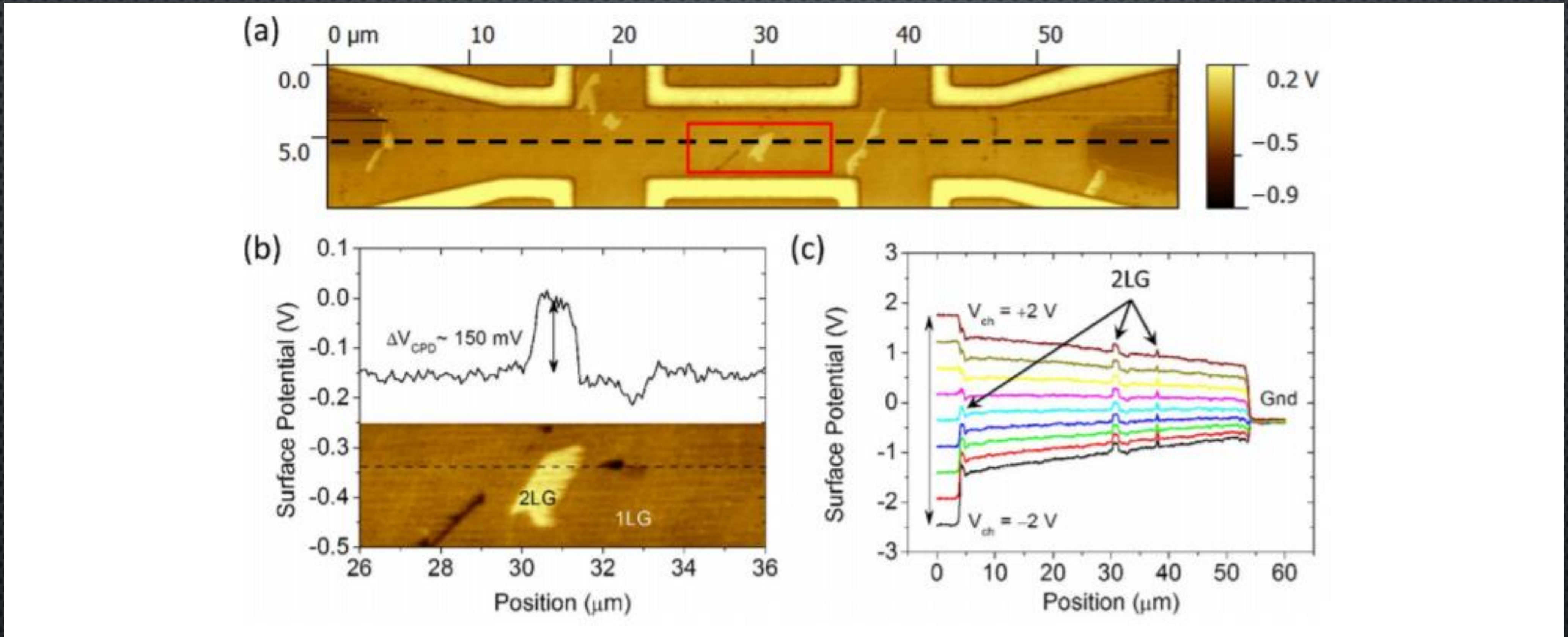
The contact potential difference (CPD) is the difference between the KPFM tip and sample work functions,
$V_{CPD} = \varphi_{tip} - \varphi_{sample}$.

The work function of the Pt/Ir tip is estimated to be 4.89 ± 0.1 eV.

The work functions of graphene and WS_2 are estimated to be 4.85 eV and 5.04 eV, respectively.

ACS Nano 2017, 11, 2785

Standardization of potential measurements for graphene domains



KPFM to study surface potential of single layer graphene (1LG) and bi-layer graphene (2LG)

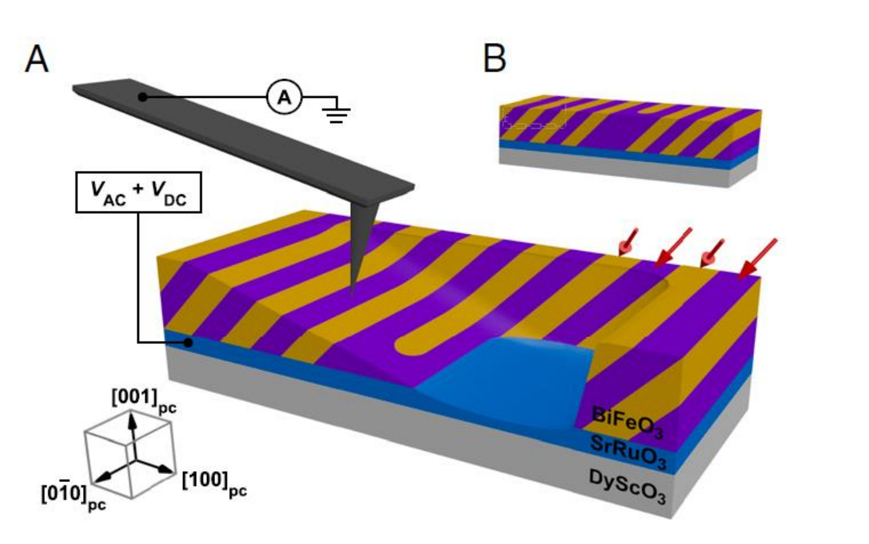
Scientific Reports, 2013, 3, 2597

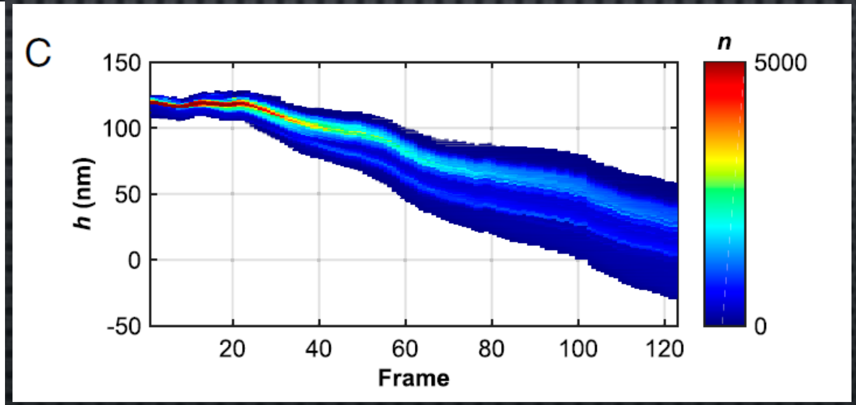
MANIPULATIONS OR IN-SITU MEASUREMENTS

Tomographic atomic force microscopy (TAFM)

TAFM is the process in which a scanned probe, with downforces as high as micronewtons, performs mechanical removal (machining) of a specimen surface while simultaneously or sequentially recording one or more imaging modes, e.g., topography and PFM.

TAFM of a $BiFeO_3/SrRuO_3/DyScO_3$ thin-film heterostructure.



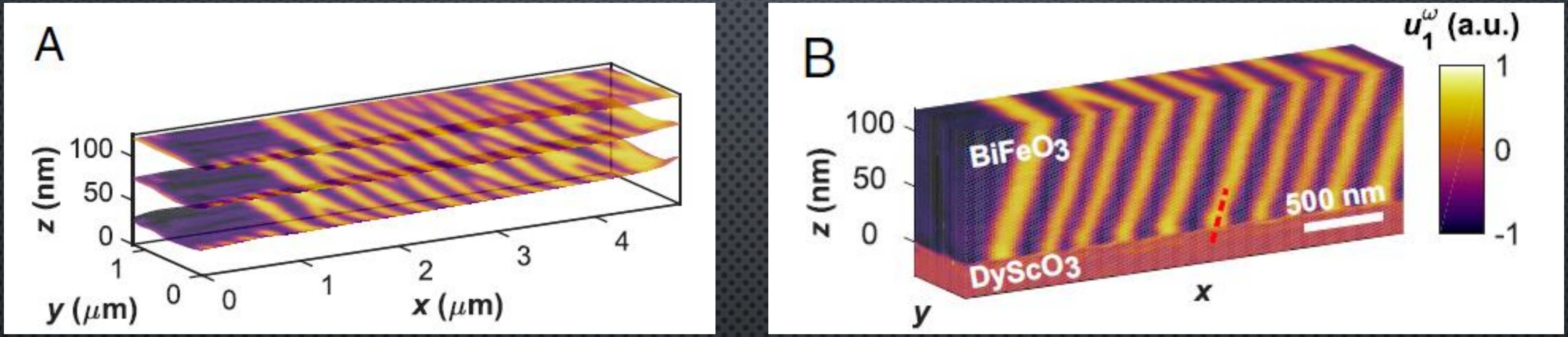


Two-dimensional histogram of z position as a function of imaging frame during TAFM of an h = 120 nm $BiFeO_3$ thin film

- 120-nm thick $BiFeO_3$ thin-film heterostructure
- 11.4-μN mean probe downforce
- Mean vertical removal rate of 0.97 nm per frame
- An overall tomographic sequence of ~200 imaging frames

PNAS, 2019, 116, 2413

Tomographic reconstruction of ferroelectricity from a $BiFeO_3$ thin-film heterostructure



PNAS, 2019, 116, 2413

Twist angle of MoS_2/Graphene heterojunctions

Twist angle between the two individual layers plays a crucial role in tuning the heterostructure properties

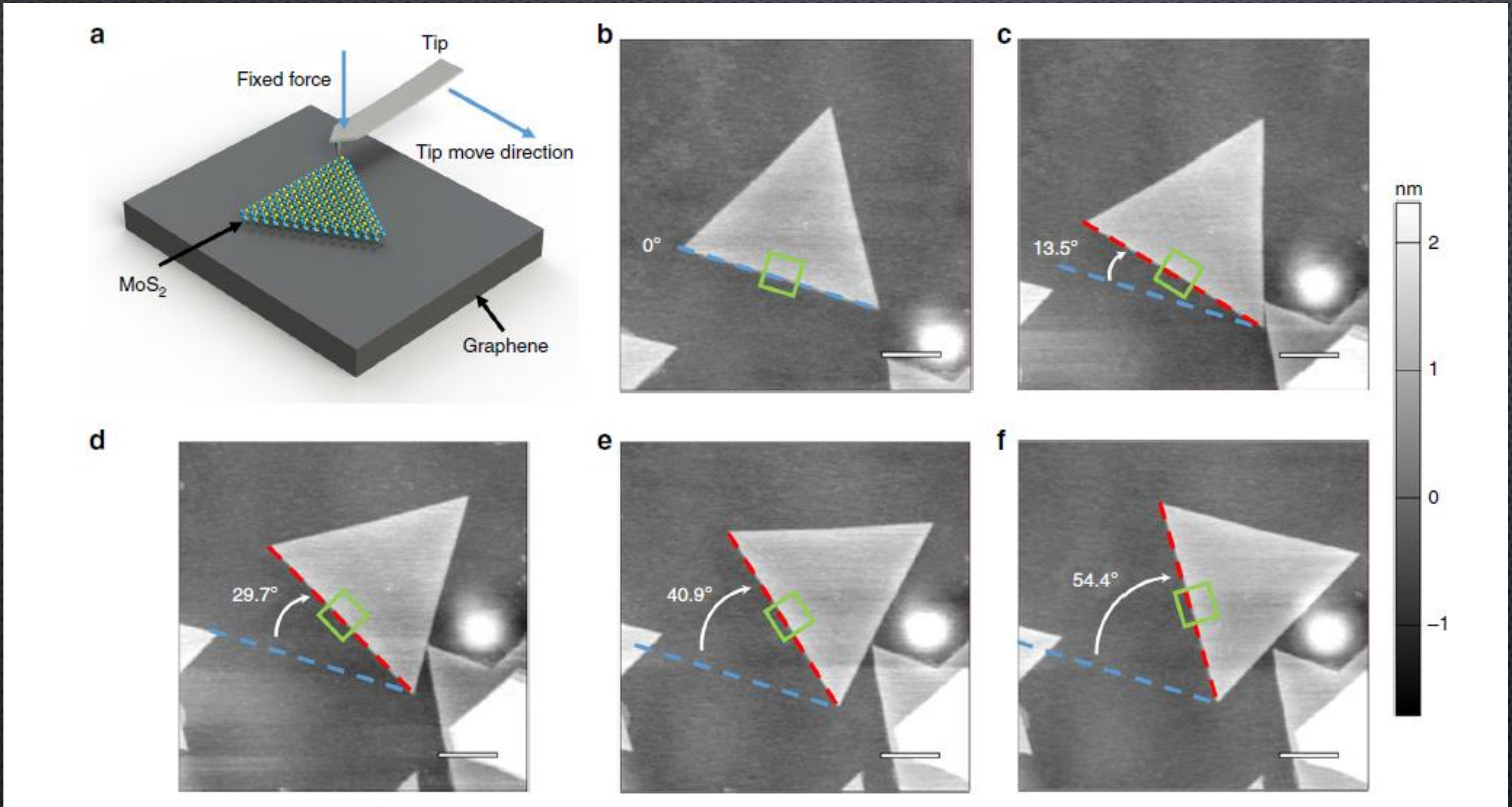
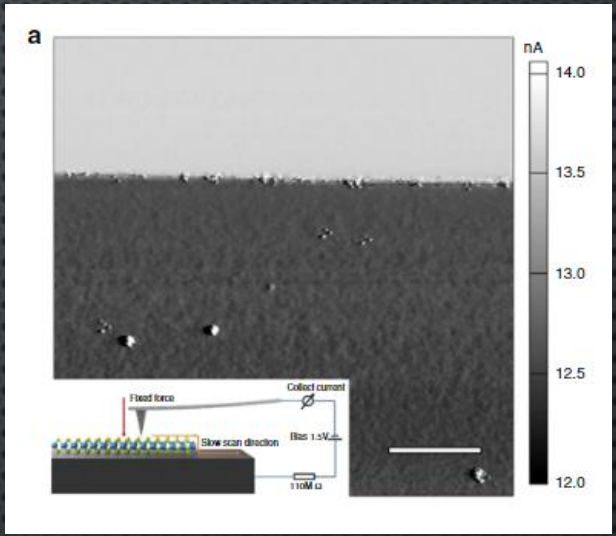
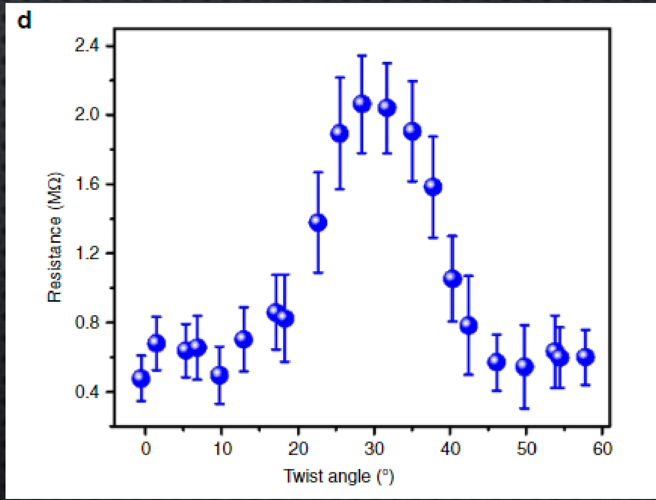


Fig. 2 Rotation of as-grown MoS_2 domains on graphene substrates. **a** Schematic of AFM-tip manipulation setup. **b–f** AFM images of a typical MoS_2 domain rotated on graphene to achieve a series of twist angles, scale bar, 1 μm. Blue dash lines indicate the original direction of the MoS_2 domain, while white arrows indicate the rotation directions. Green rectangles represent the scan area during C-AFM measurements

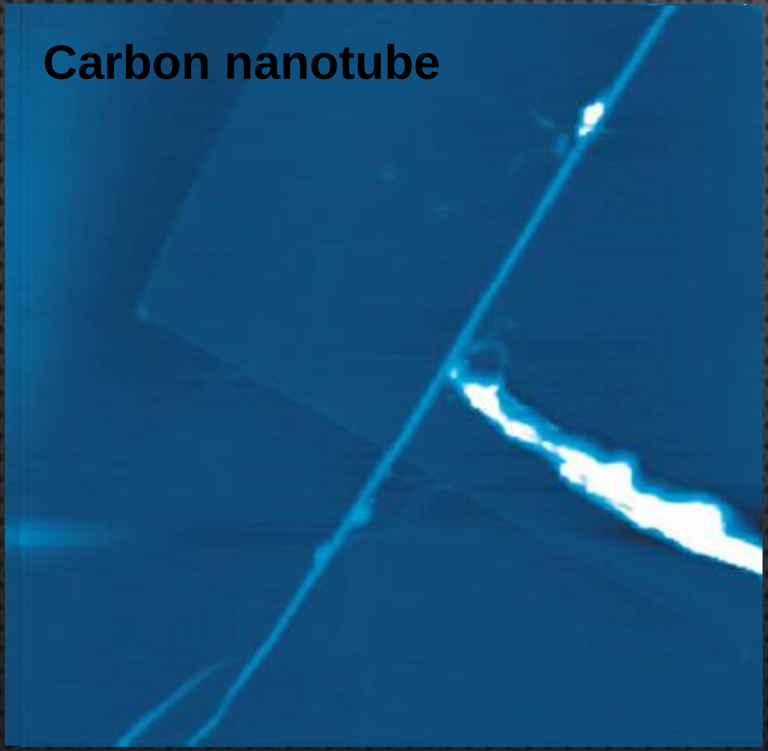


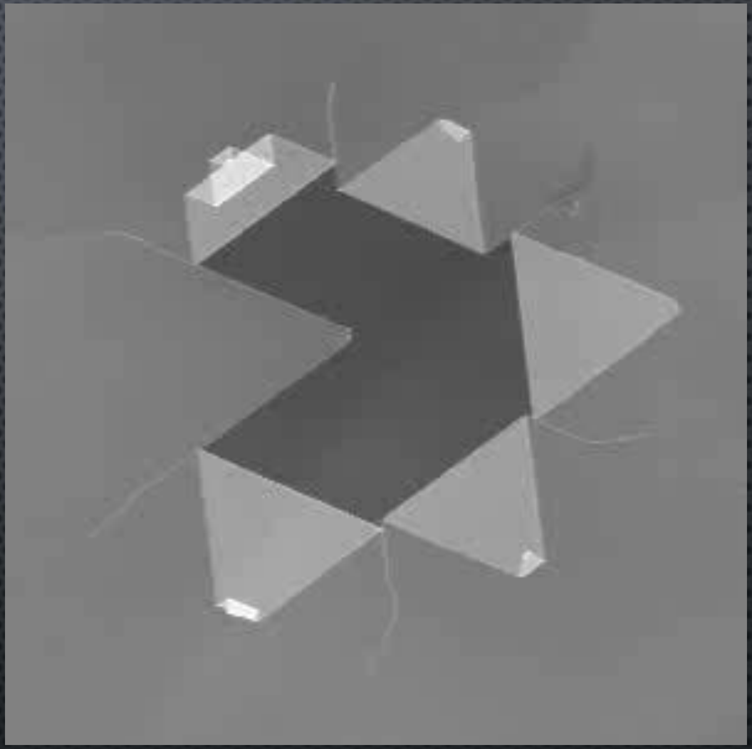


- **Manipulate MoS_2 on graphene substrate using AFM probe**
- **Measure electrical properties using CAFM for each angle**

Nat. Comm., 2018, 9, 4068

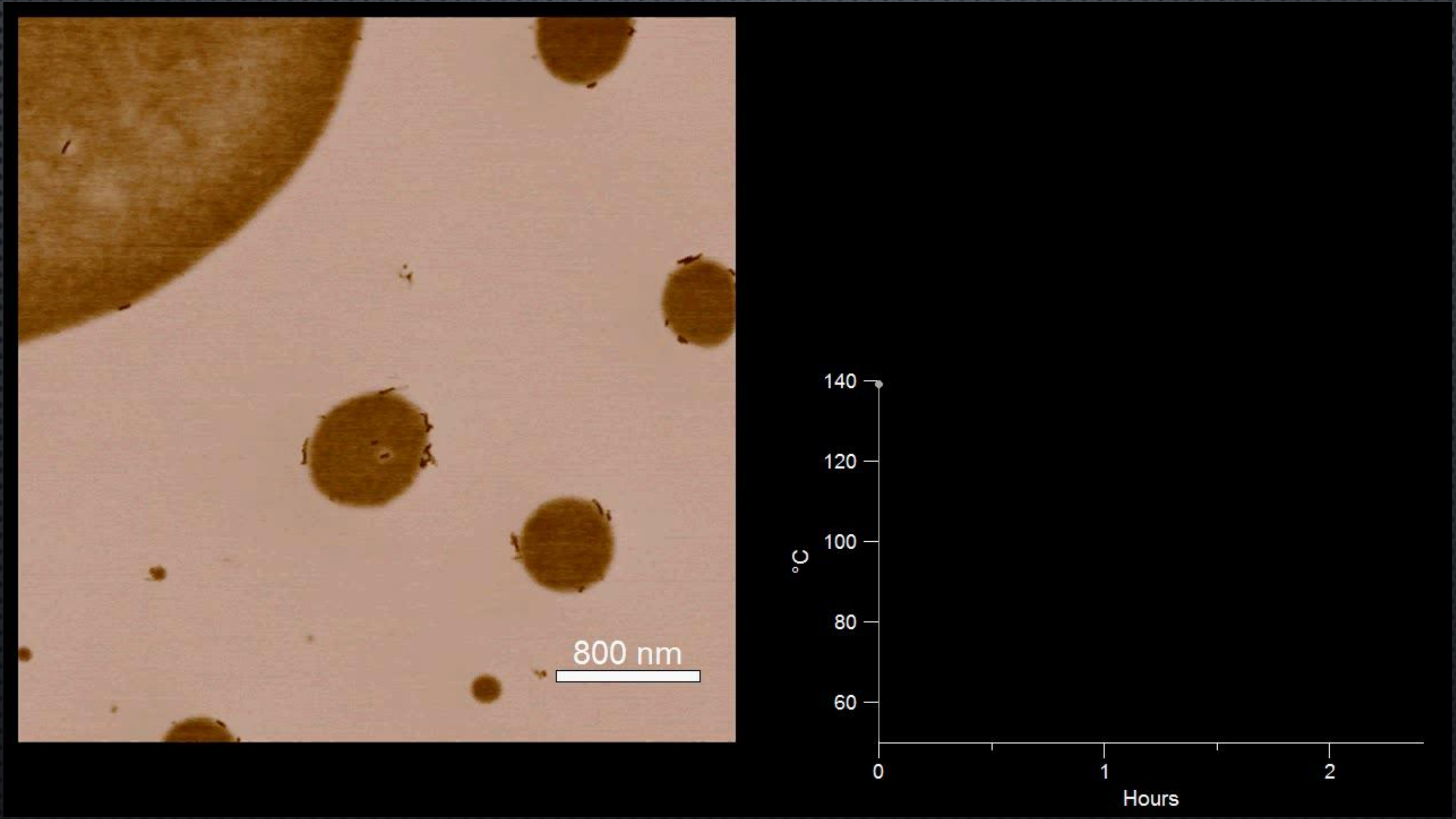
Nanomanipulation





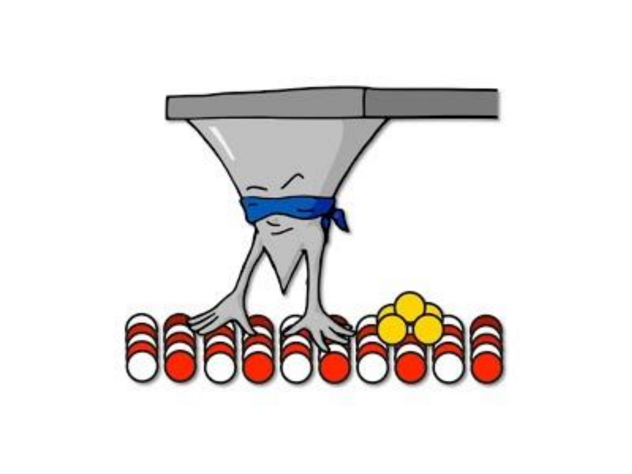
-Asylum research gallery

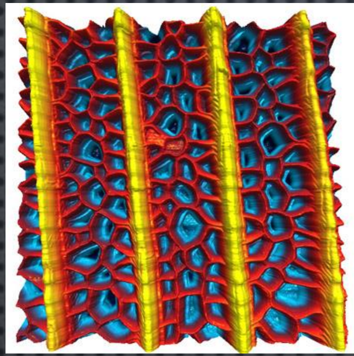
In-situ characterization
Heating / Cooling of syndiotactic polypropylene - polystyrene (sPP-PS) on Silicon

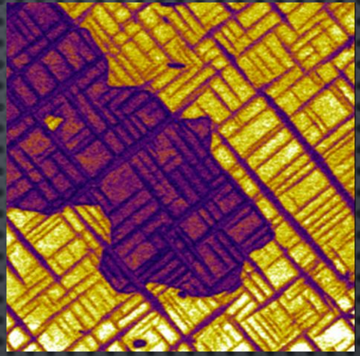


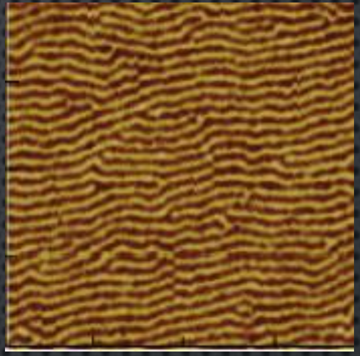
-Asylum research gallery

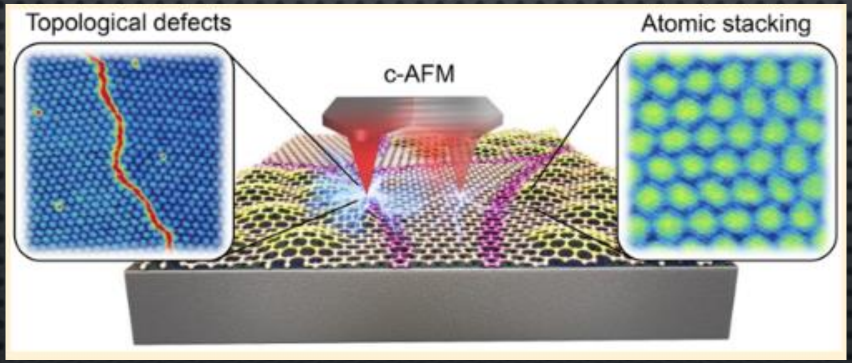
SUMMARY

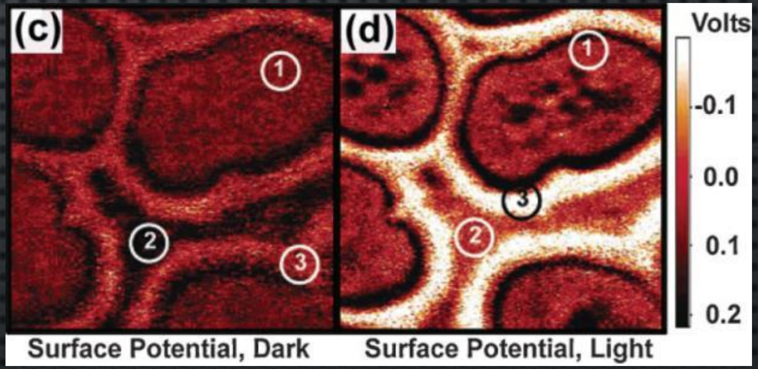


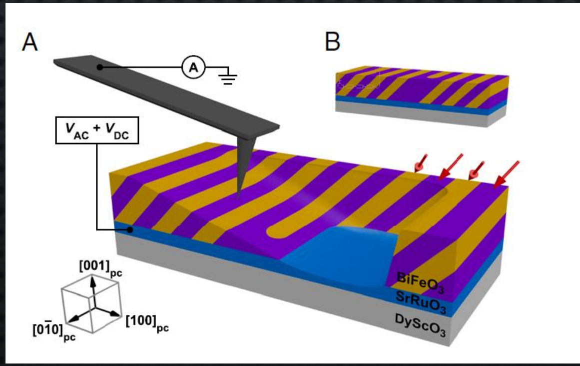


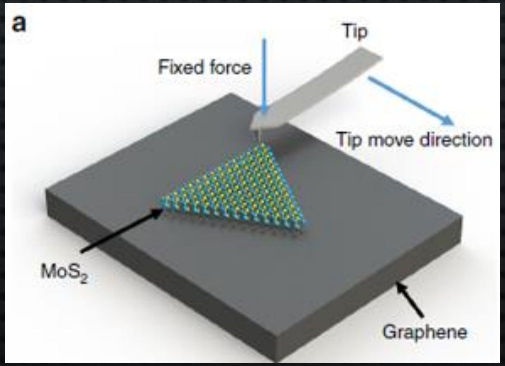


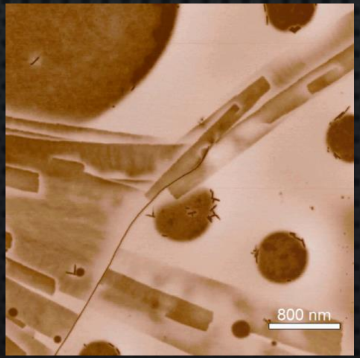



Topological defects
c-AFM
Atomic stacking


(c)
(d)
Volts
-0.1
0.0
0.1
0.2
1
2
3
Surface Potential, Dark
Surface Potential, Light


A
B
A
$V_{AC} + V_{DC}$
$BiFeO_3$
$SrRuO_3$
$DyScO_3$
$[001]_{pc}$
$[100]_{pc}$
$[0\bar{1}0]_{pc}$


a
Tip
Fixed force
Tip move direction
MoS_2
Graphene


800 nm

QUESTIONS?

Thank you for your attention !

peggy.zhang@unsw.edu.au

APPLICATIONS

nature chemistry
ARTICLES
https://doi.org/10.1038/s41557-018-0170-0

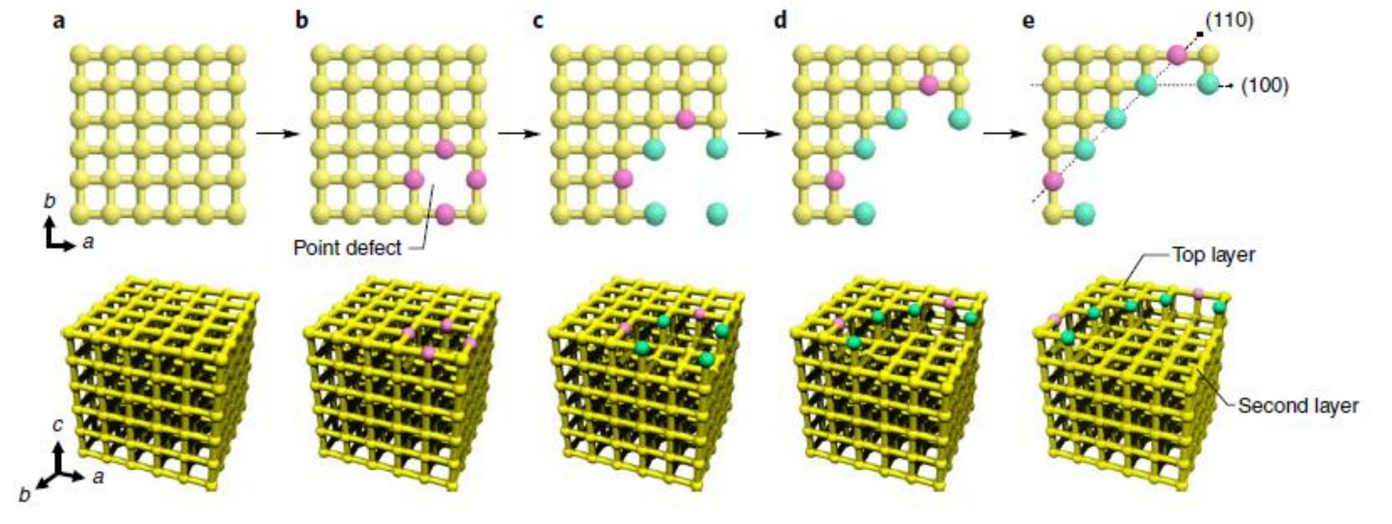
Highly responsive nature of porous coordination polymer surfaces imaged by in situ atomic force microscopy

Nobuhiko Hosono[1,2*], Aya Terashima[1], Shinpei Kusaka[1,3], Ryotaro Matsuda[1,3] and Susumu Kitagawa[1*]

Experiment set-up

- AFM micrographs were taken at 28 °C using an Asylum Research (Oxford Instruments) model Cypher ES equipped with BlueDrive photothermal excitation.
- Tapping mode phase with Cypher ES and blueDrive at 19.5 Hz line scan rate (~13 s per image)

Delamination of Porous coordination polymers (PCPs) crystals -- $(Zn2(1,4\text{-}ndc)_2(dabco))_n$



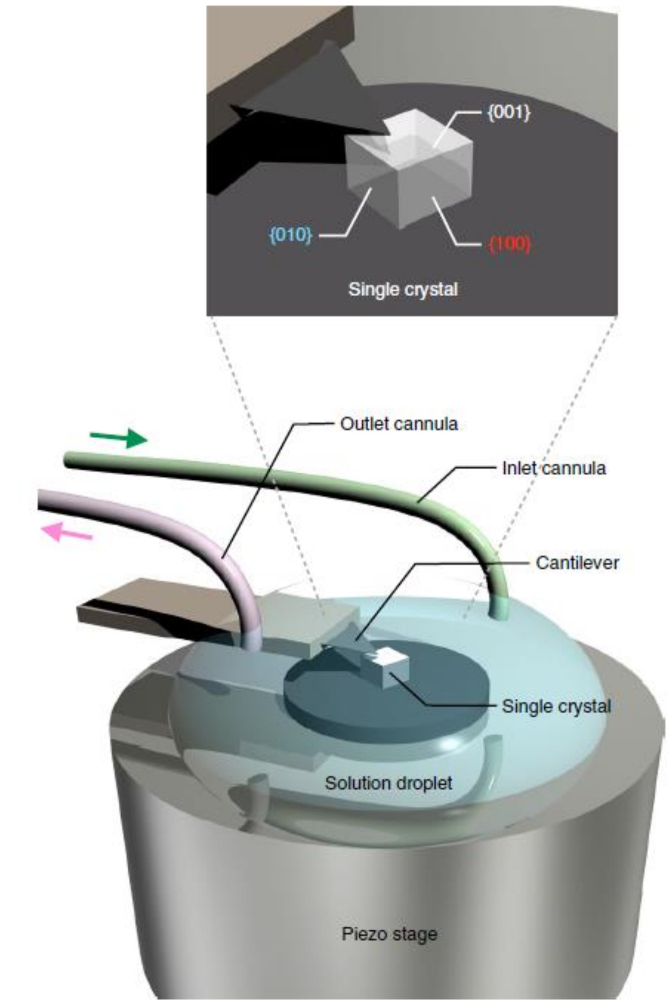
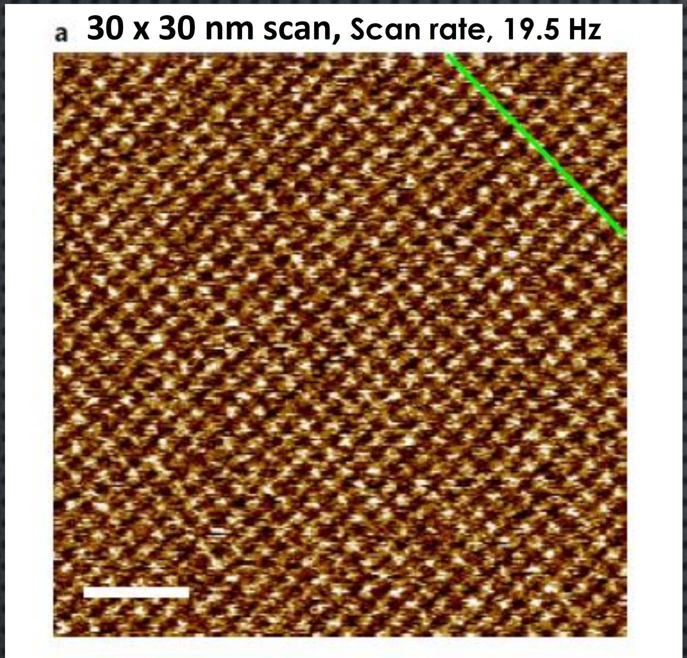
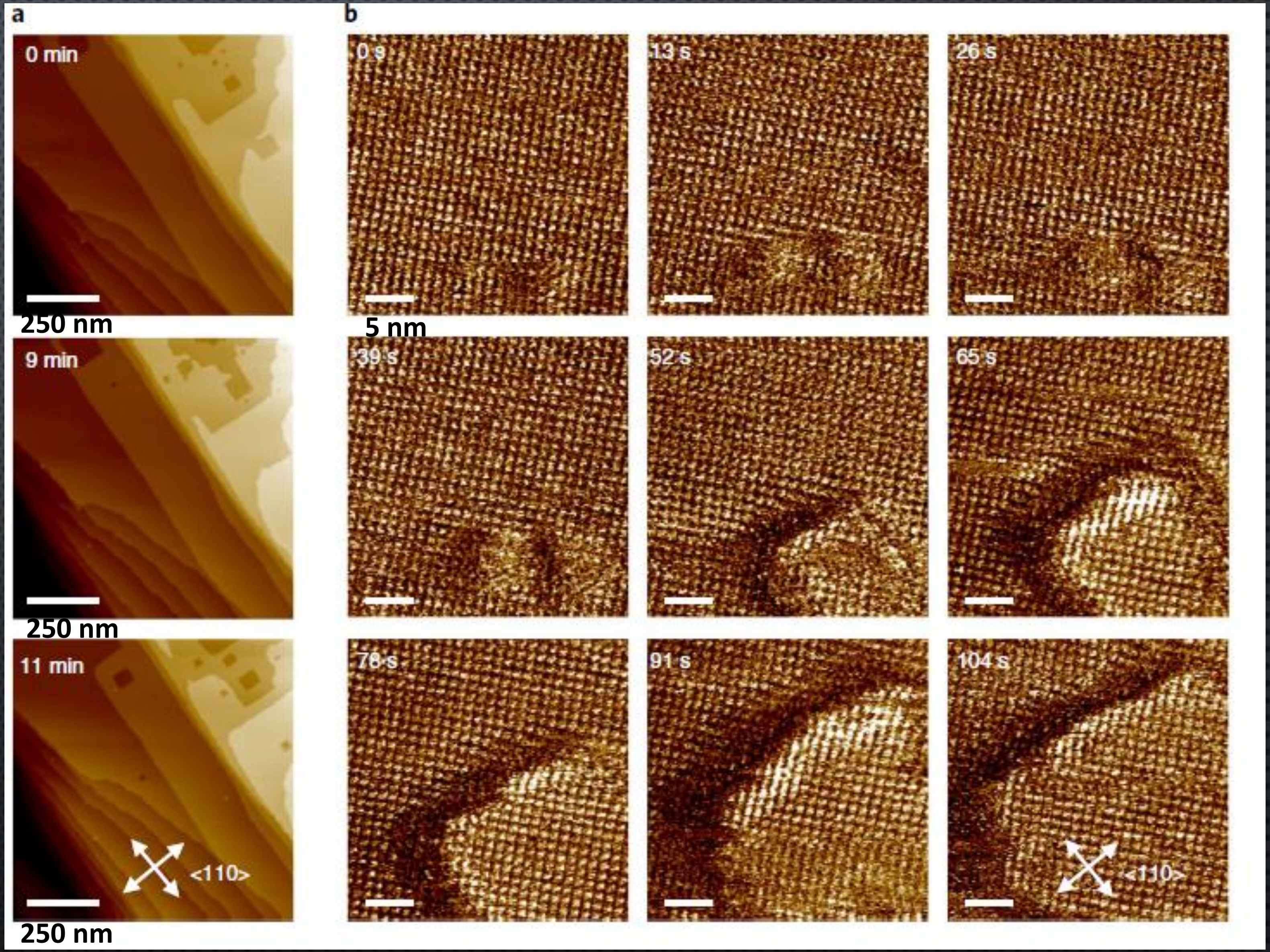


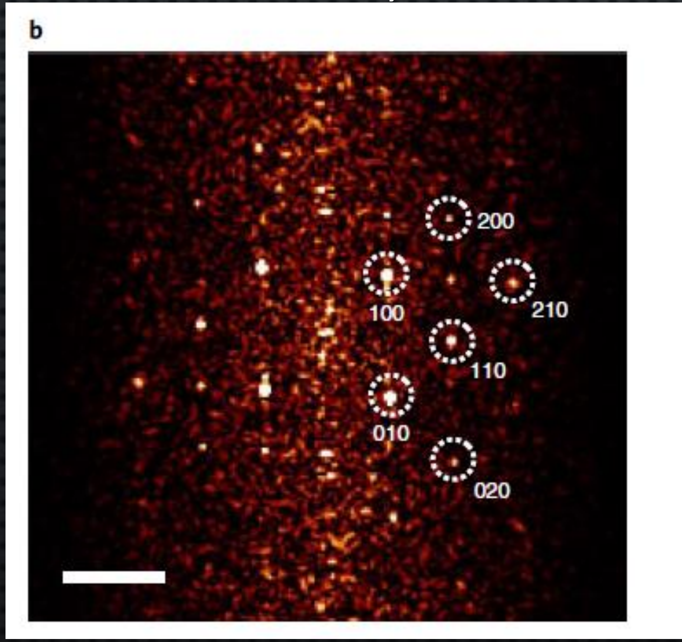
Fig. 2 | Experimental set-up for in situ AFM imaging. Schematic illustration of the experimental set-up for in situ AFM imaging with perfusion flow of the guest solution. A single crystal of **1** was taken from the DMF solution and placed in the solution droplet where the objective facet was selected to be the top surface. The droplet solution is in contact with the inlet and outlet cannulas and exchanged with the guest solution by perfusion flow at a constant rate of 60–70 μl min⁻¹.



Layer-by-layer delamination process captured in situ at the lattice scale



2D FFT spectrum of the real image
Scale bar, 1 nm^{-1}.



With exfoliation of the first layer, the second layer appears and develops along the < 110> direction

NANO LETTERS

Letter

Cite This: *Nano Lett.* XXXX, XXX, XXX−XXX

pubs.acs.org/NanoLett

Barrier Inhomogeneities in Atomic Contacts on WS_2

Krystian Nowakowski,[†] Harold J. W. Zandvliet,[†] and Pantelis Bampoulis*[,†,§]

[†]Physics of Interfaces and Nanomaterials, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500AE Enschede, The Netherlands

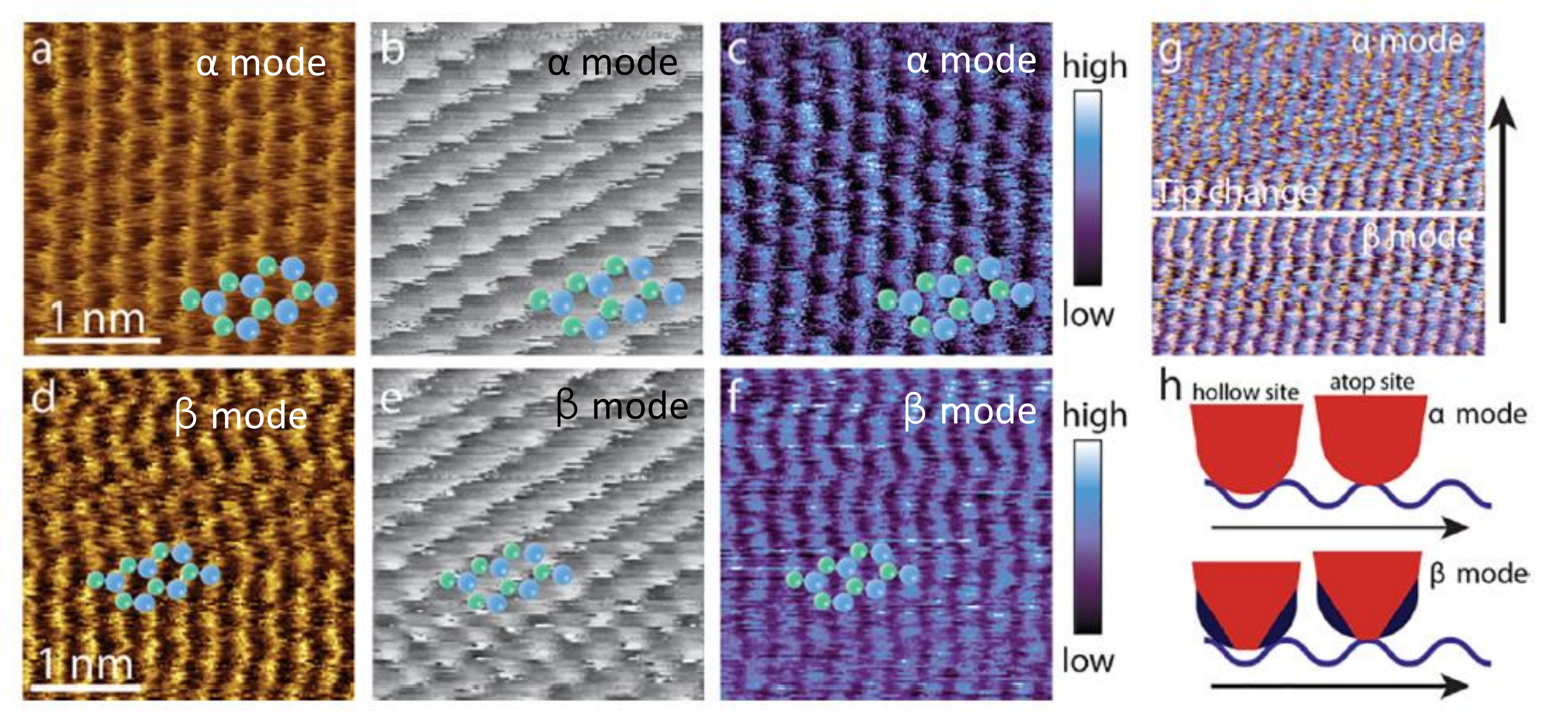
[§]Physikalisches Institut, Universität zu Köln, Zülpicher Straße 77, 50937 Köln, Germany

Nano Lett. 2019, 19, 2, 1190

Study surface conductivity of Tungsten disulfide (WS_2) using c-AFM.

C-AFM can provide true atomic resolution on atomically smooth semiconductor surfaces, such as WS_2,by utilizing **quantum point contact microscopy**.

(a) Topography (b) LFM (c) CAFM



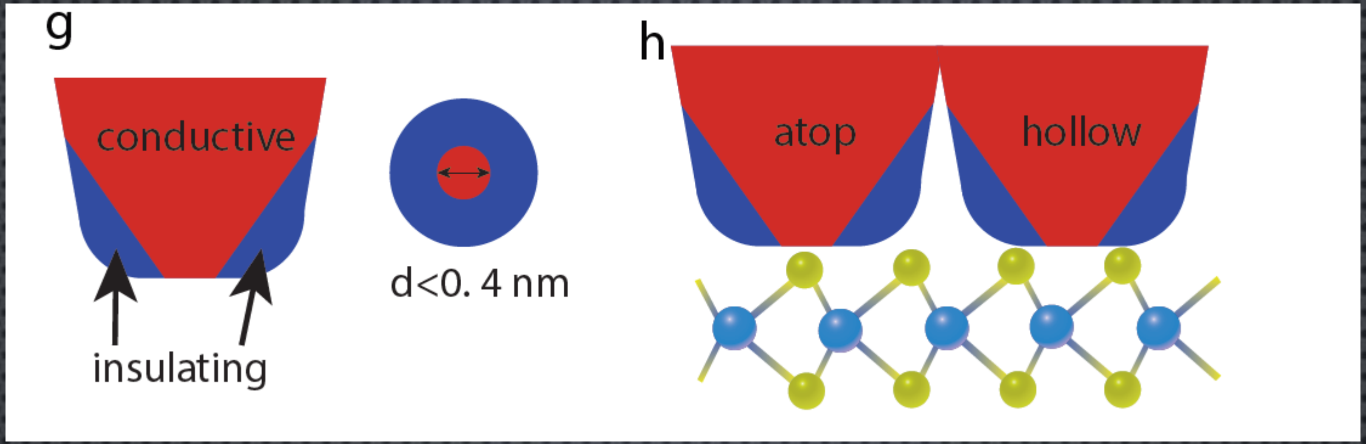
- Lattice periodicity
- Conductivity

Probe:

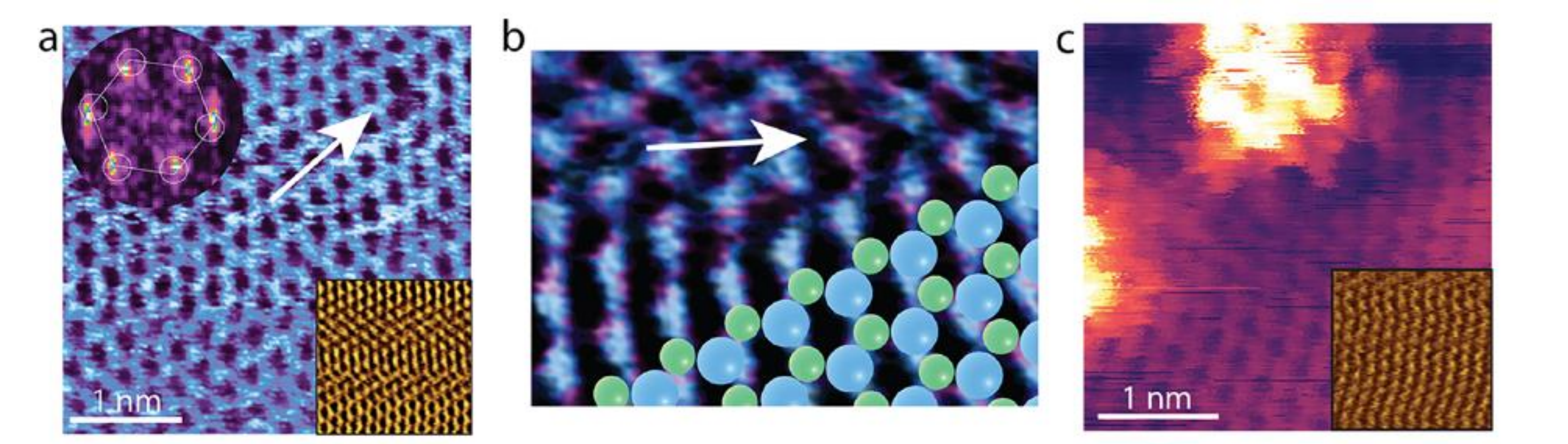
- highly conductive p-type doped diamond tips
- spring constant of 0.5 N/m and radius of curvature below 5 nm.

- α mode: fully conductive tip
- β mode: partially insulating tip

β mode



β mode

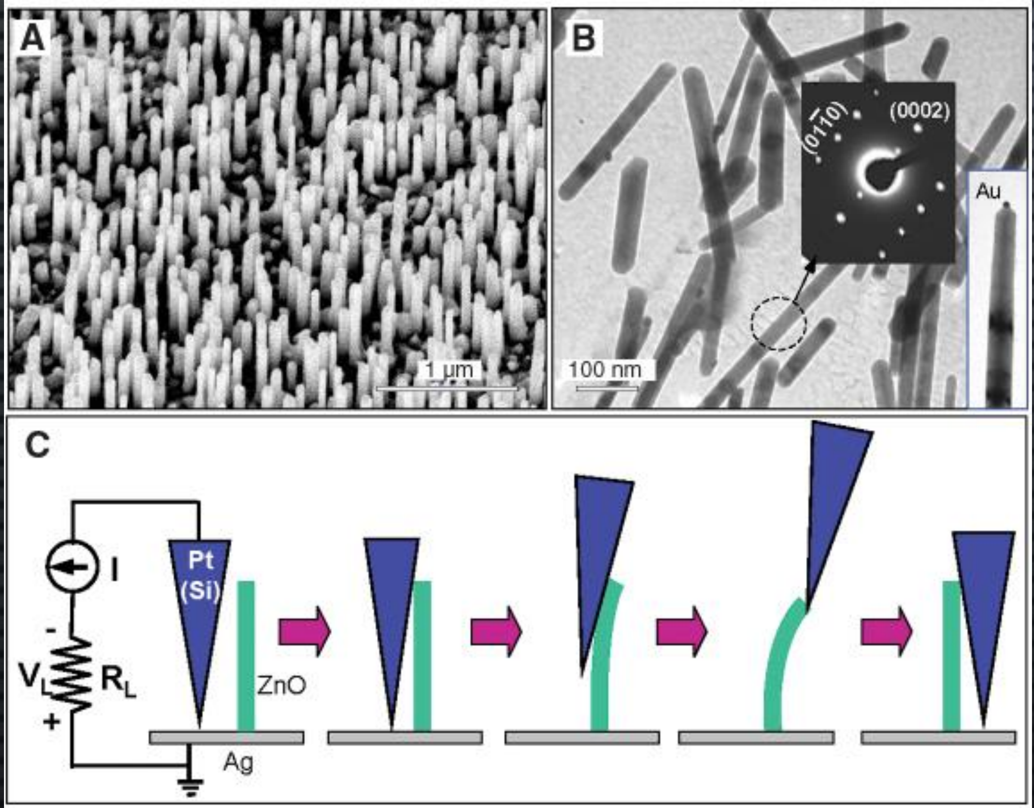


- Current image of WS_2 surface **showing a chalcogen vacancy** (indicated by the arrow).
- Current image containing other type of surface defects having a large electronic influence in their surroundings.

Nano Lett. **2019, 19, 2, 1190**

CAFM APPLICATIONS

- TO STUDY PIEZOELECTRICITY



Science 312.5771 (2006): 242-246.

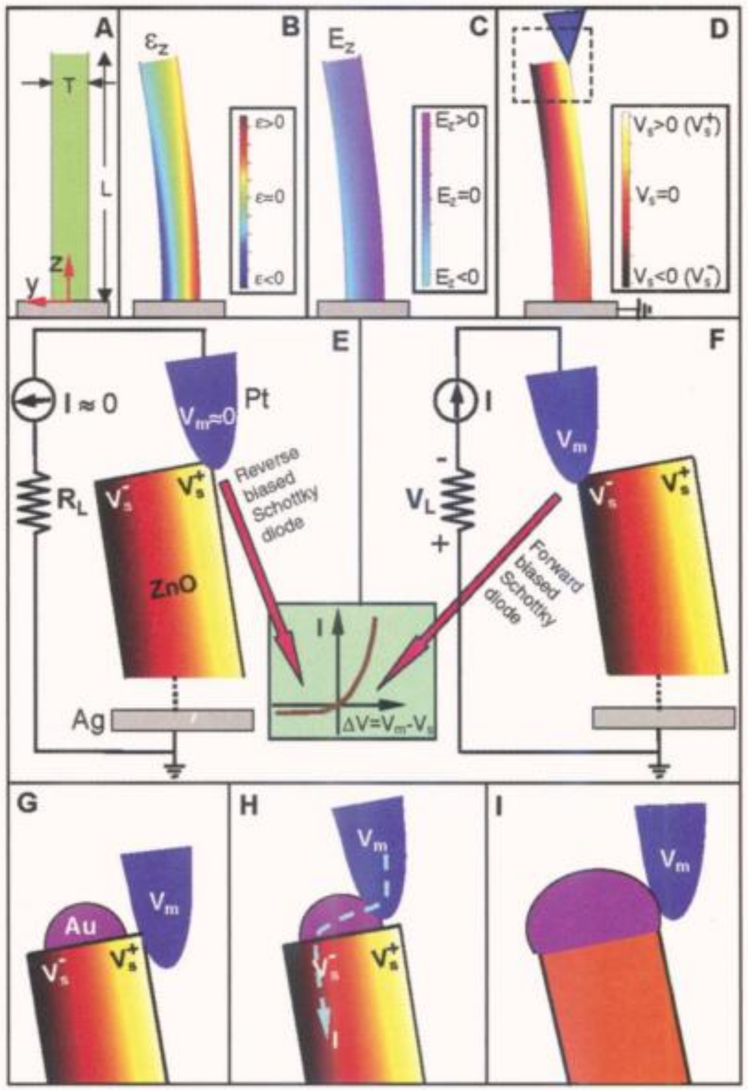
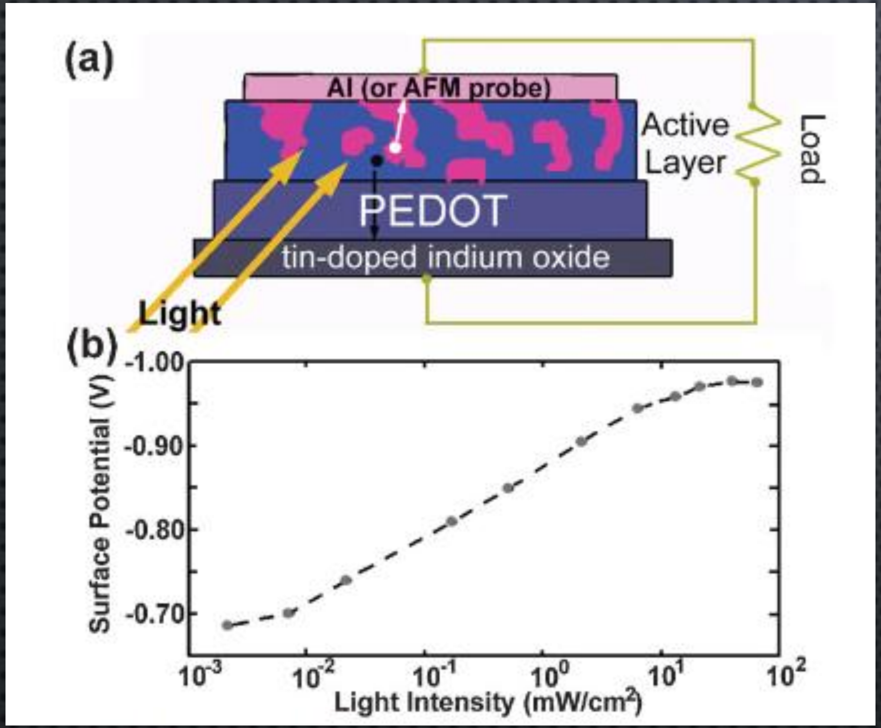
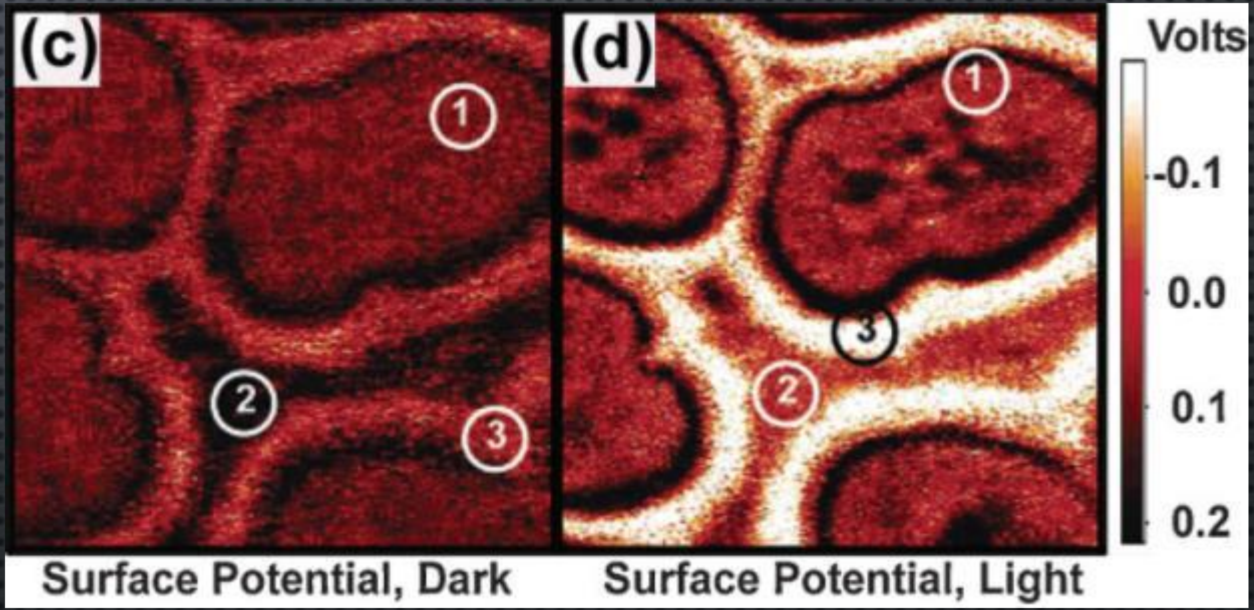


Fig. 3. Transport is governed by a metal-semiconductor Schottky barrier for the PZ ZnO NW (see movies S1 and S2). (**A**) Schematic definition of a NW and the coordination system. (**B**) Longitudinal strain ε_z distribution in the NW after being deflected by an AFM tip from the side. The data were simulated by FEMLAB for a ZnO NW of length 1 μm and an aspect ratio of 10. (**C**) The corresponding longitudinal PZ-induced electric field E_z distribution in the NW. (**D**) Potential distribution in the NW as a result of the PZ effect. (**E** and **F**) Contacts between the AFM tip and the semiconductor ZnO NW [boxed area in (D)] at two reversed local contact potentials (positive and negative), showing reverse- and forward-biased Schottky rectifying behavior, respectively (see text). This oppositely biased Schottky barrier across the NW preserves the PZ charges and later produces the discharge output. The inset shows a typical current-voltage (*I-V*) relation characteristic of a metal-semiconductor (n-type) Schottky barrier. The process in (E) is to separate and maintain the charges as well as build up the potential. The process in (F) is to discharge the potential and generates electric current. (**G** and **H**) Contact of the metal tip with a ZnO NW with a small Au particle at the top. The PZ potential is built up in the displacing process (G), and later the charges are released through the compressed side of the NW (H). (**I**) Contact of the metal tip with a ZnO NW with a large Au particle at the top. The charges are gradually "leaked" out through the compressed side of the NW as soon as the deformation occurs; thus, no accumulated potential will be created.

Photoelectric conversion

Polymer blend (F8BT:PFB)





- Investigate the surface potential change with light using KPFM

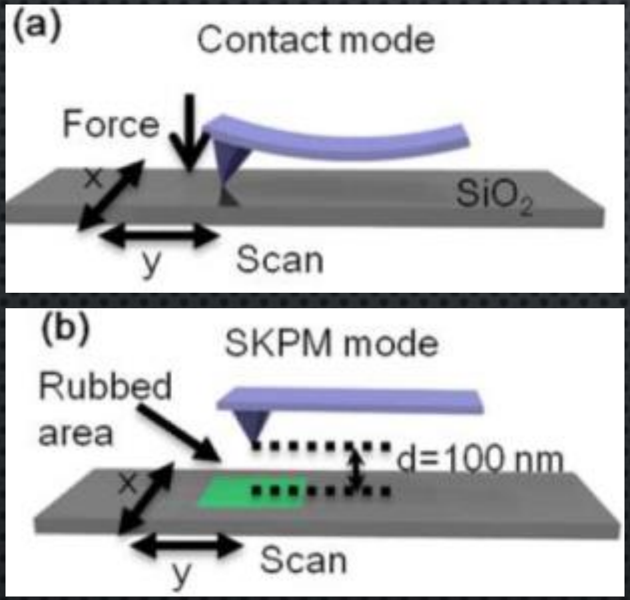
NanoLett.2005,5, 559

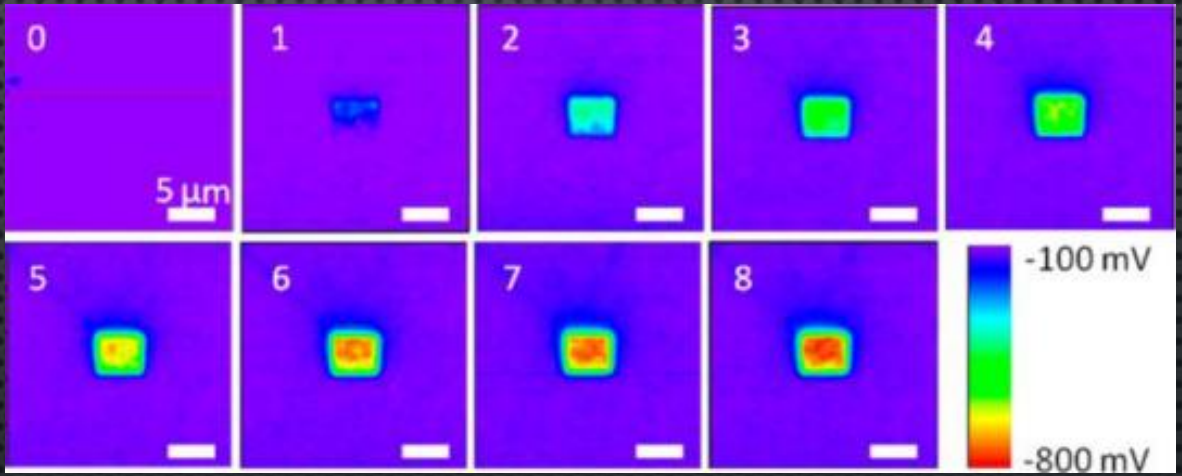
Advanced Materials 21.1 (2009): 19-28.

KPFM APPLICATION

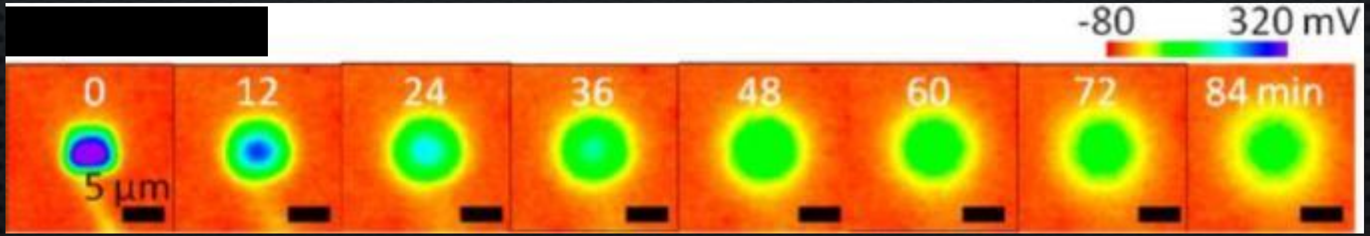
- Research on Triboelectric generators （Prof. Zhonglin Wang）

Increase of the number of repeated rubbing at the same area @120 nN





Series of images of surface potential distribution as a function of time after the triboelectrification



Nano letters 13.6 (2013): 2771-2776.