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# Principle of Electrostatic Force Microscopy and Applications

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- I Introduction
- II Electrostatic Force Microscopy (EFM)
- III Kelvin Probe Force Microscopy (KPFM)



#### I – Introduction



### A few motivations

#### EX 1 : Imaging the operation of CNT-FETs as charge sensors

[D. Brunel et al., ACS Nano 2010]



#### **EX 2 : coupled CNTFETs and nanocrystals**



## A few motivations

**EX 3 : photovoltaic materials** 



P3HT:PCBM blend molecular D/A junction





#### cf Ł. Borowik / B. Grévin

#### EFM

#### **Electrostatic Force Microscopy**

Measurement of electrostatic force gradients

Units : Hz or N/m

#### KPFM

#### **Kelvin Probe Force Microscopy**

Compensation of electrostatic forces

Units : V

**Charge detection** 



Probing local surface potentials



#### **Basics**



#### **Charge detection**



charges in vacuum → charges in a capacitor



# Charge {≡ capacitance}







Energy stored in a capacitor  $\frac{1}{2}$  C V<sup>2</sup>

Attractive force between capacitor plates

$$F_{z} = + \frac{1}{2} \frac{dC}{dz} V^{2} (<0)$$





#### **Electrostatic Force { Electrostatic Force**





#### **Force gradient detection**

$$F_z = F_z(z_0) + (z-z_0) \cdot F'_z(z_0)$$

frequency shift : df= -  $f_0/2k$ .  $F'_z(z_0)$ 

- Here: long-range forces [ambient air / UHV]
- Short-range electrostatic forces disregarded here



#### Force gradient {= capacitance 2<sup>nd</sup> derivative}



#### We could almost stop the presentation now ...

- due to tip apex size → sensitivity to few or single charge events provided the signal to noise ratio is sufficient
- typically sub-pN forces or 10<sup>-5</sup> N/m force gradients (z=100nm)
- force gradients at the tip apex can exceed force gradients at the cantilever

Frequency Modulation (FM) modes already appear better than Amplitude Modulation (AM) modes with this respect



#### **II - Electrostatic Force Microscopy**



### capacitive forces



## **Capacitive forces 1/2**

#### Capacitive signals associated with topgraphic features



EFM (frequency shift) image

**Topography image** 



z scale

50 nm

freq. scale 40 Hz

## **Capacitive forces 2/2**

#### **Capacitive signals associated with sub-surface nanostructures**



Fig. 4.6. (a) Schematic illustration of the polymer/SWCNT sample and EFM operation. (b) Topography image of the 60 nm-thick film of PMMA/SWCNT composite. Because of the polymer, the tubes cannot be observed. (c) Corresponding EFM image (tip-substrate distance h = 35 nm, tip biased at +7 V), in which individual SWCNTs are clearly seen as dark lines (negative phase shifts). Adapted from [23]

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J. Nygard et al. Appl. Phys. Lett. 90 183108 (2007)

## charge manipulation



### **Charge manipulation**



#### AFM Image 2500 x 2500 nm<sup>2</sup>

#### Contact force : a few nN Charge retention time : of few 10 min (dry N<sub>2</sub>)



## Imaging charged nanocrystals





Appl. Phys. Lett., 78 5054 (2002)

#### electrostatic force analysis



#### **Electrostatic forces**



Isopotential map of a charged dielectric sphere with grounded substrate and tip



#### **Electrostatic forces**





#### **Electrostatic forces**





#### **Charge screening**





## **Two opposite situations**





### **Electrostatic forces without energy diagrams**



charged nanoparticle (V=0)

#### dipole-dipole interaction $\,\,\alpha\,\,Q^2$



## **Electrostatic forces without energy diagrams**



 $+Q_{c}$ 

charged nanoparticle (V=0)

uncharged nanoparticle ( $V \neq 0$ )



dipole-dipole interaction  $\alpha Q^2$ 

capacitive interaction  $\alpha$  V²

## **Electrostatic forces without energy diagrams**



charged nanoparticle (V=0) charged nanoparticle (V $\neq$ 0V) uncharged nanoparticle (V $\neq$ 0)



dipole-dipole interaction  $\alpha Q^2$ dipole-charge interaction  $\alpha Q.V$ capacitive interaction  $\alpha V^2$ 

## Experimental spectroscopic analysis [here : screened charges above a conducting plane]



#### Spectroscopic analysis of charge signals



## dipole-dipole interactions



2z

## **Charges or dipoles ?**



## Probing a charge or a dipole ?



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#### Probing a charge or a dipole ?


# Probing a charge or a dipole ?



### Probing a charge or a dipole ?





[MWCNT with 18 nm diameter,  $V_{inj}$ =-7V (3 min) detection  $V_{EFM}$ =-3V]



#### image force contributions



#### Apparent topography due to image forces



Figure 3.2: Charging of ion implanted samples-unetched.



E. Boer et al. - APL (2002)

#### Apparent topography due to image forces



#### Charge injection in a 7nm thick SiO<sub>2</sub> layer



R. Dianoux, PhD (2004)

#### **Missing points**

- sensitivity
- spatial resolution
- time resolution
- quantitative charge measurements ?



#### Sensitivity

# Optical beam deflection EFM with soft cantilevers (k=3N/m;f<sub>0</sub>=60kHz)

	in air	in vacuum, 300K	
	limited by thermal noise		
F' <sub>min</sub>	<b>~10<sup>-5</sup> N/m</b> B=100Hz, Q=200 A=25nm	<b>a few 10<sup>-6</sup> N/m</b> B=50Hz, Q=20000 A=15nm	
<z></z>	50-100nm	10-20nm	

$$F'_{min} = \sqrt{\frac{4 \text{ k} \cdot \text{k}_{\text{B}} \text{T} \cdot \text{B}}{\pi \text{ f}_{0} \cdot \text{A}^{2} \cdot \text{Q}}}$$



[F. Giessibl et al., Phys. Rev. B 2011 + references therein]

#### Sensitivity

Optical beam deflection EFM with soft cantilevers (k=3N/m;f<sub>0</sub>=60kHz)

Qplus, LER

	in air	in vacuum, 300K	vacuum, 1-5 K
	limited by thermal noise		deflection noise, thermal noise,
F' <sub>min</sub>	<b>~10<sup>-5</sup> N/m</b> B=100Hz, Q=200 A=25nm	<b>a few 10<sup>-6</sup> N/m</b> B=50Hz, Q=20000 A=15nm	<b>~ 10<sup>-3</sup> N/m</b> B=25Hz, Q=20000 A=200pm
<z></z>	<b>50-100nm</b>	10-20nm	< 1 nm
	Long-range (LR)	LR + SR	Short-range (SR)



# single charge detection in air



## **ω/2ω EFM**



three force  
components
$$\begin{cases}
static & F'_{0\omega} = \frac{1}{2} d^2 C/dz^2 \left[ (V_{dc} - V_s)^2 + V_{ac}^2/2 \right] & \text{not desired here} \\
\omega & F'_{\omega} = d^2 C/dz^2 \left( V_{cc} V_s \right) V_{ac} \cos(\omega t) & zero \text{ if } V_{dc} = V_s \\
2\omega & F'_{2\omega} = \frac{1}{4} d^2 C/dz^2 V_{ac}^2 \cos(2\omega t) & capacitive interaction
\end{cases}$$

#### **ω/2ω EFM**



For  $V_{ds}=V_s$ , a surface charge Q will :

- interact with its image charges
- interact with ac charges at the tip

Separation of charge and dielectric images

three force  
components
$$\begin{cases}
static & F'_{0\omega} = \frac{1}{2} d^2 C/dz^2 \left[ (V_{dc} - V_s)^2 + V_{ac}^2/2 \right] + \text{image force contributions} \\
\omega & F'_{\omega} = d^2 C/dz^2 \left( \sqrt{V_{cc}} V_s \right) V_{ac} \cos(\omega t) + K(z) \cdot Q \cdot CV_{ac} \cos(\omega t) \\
2\omega & F'_{2\omega} = \frac{1}{4} d^2 C/dz^2 V_{ac}^2 \cos(2\omega t) \quad \text{(no change)}
\end{cases}$$

#### Single charge detection in ambient air



# Single-charge sensitivity with sub-nm resolution

2009

Δz

[4K AFM]

1999 Columbia Univ., *Phys. Rev. Lett.* 

#### [ac-modulated EFM in air]



Single charge fluctuations in CdSe nanocrystals

#### resolution 25nm

# etric image

# Single charge state of Au adatoms

IBM Zürich, Science

0.0

-0.5

-1.0

-1.5

-2.0

Au⁰

20

10

∆f (Hz)

resolution < 1nm [UHV et 4K] **Figure 1:** (from [2]) Left: schematics of nc-AFM with sub-nm tip oscillation, here on Au adatoms on an ultra-thin NaCl layer. Right: tuning-fork frequency shifts above two adatoms (5K). The contrast difference between the Au0 and Au-adatoms corresponds to a single charge.

Au

40

30

Lateral Distance (Å)

50



#### **Time resolution**

- in general, limited by the phase demodulation of the cantilever oscillation
- better resolution possible :
  - fast frequency shift demodulation,
  - oscillation transients (sub-µs see D. Ginger et al. Nanoletters 2012)
  - response under modulated illumination (see Ł. Borowik)

# **Quantitative charge measurements ?**

- in general, semi-quantitative models only
- difficult due to the large variety of dielectric environments
- numerical simulations in most situations
- single charge events as calibration



#### **III - Kelvin Probe Force Microscopy**

#### surface potential and charge detection



#### Principle ...



different metals

#### Measuring surface potentials from forces

- Lord Kelvin (1898)
- Zisman (1932) : vibrating Kelvin probe (down to mm size)
- Nonnenmacher (1991) : Kelvin probe force microscopy





#### **Energy diagrams**









### **Energy diagrams**



- The sign of  $V_{dc}$  is user-dependent ( $V_{dc}$  at the tip, or at the sample)
- $V_{dc}$  at the tip (and  $V_s$  at the surface)

'electrostatics-friendly' convention :



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'electrostatics-friendly' convention :



- The sign of  $V_{dc}$  is user-dependent ( $V_{dc}$  at the tip, or at the sample)
- V<sub>dc</sub> at the tip (and V<sub>s</sub> at the surface)
   'electrostatics friendly' convention

   a positive charge or dipole (e.g. adsorbate) is 'seen' as a positive V<sub>s</sub>
- V<sub>dc</sub> at the sample

#### **'work-function friendly' convention** :

a material with a larger work-function will be imaged as « more positive » in KPFM images



#### **Oscillating probe**



#### A NEW METHOD OF MEASURING CONTACT POTENTIAL DIFFERENCES IN METALS

By W. A. ZISMAN

[Jefferson Physical Laboratory, Harvard University, Cambridge, Mass. Received March 5, 1932]

#### ABSTRACT

A new method is described for measuring the contact potential differences between dissimilar metals. It enables one to measure the p.d. to 1/1000 volt in a few seconds of manipulation. An apparatus is described for studying metals in air and another is described for high vacuum work.



#### **Kelvin method**

Response of the electrometer deflection as a function of  $V_{\rm dc}$  to find the zero force



# Zisman method

Rev. Sci. Instrum. 3, 367 (1932)



 $C = C_0 + \Delta C.\sin \omega t$   $\downarrow$   $i(t) = \Delta C.\omega. [V_{dc} - V_s].\cos(\omega t)$ 

to a loud speaker (!) (ω in the audio range) : zero sound for V<sub>dc</sub>= V<sub>s</sub>

# Frequency Modulation Kelvin Probe Force Microscopy (FM-KPFM)



#### **FM-KPFM**





regulating  $F'_{\omega}$  to zero (df<sub> $\omega$ </sub>=0) gives : V<sub>dc</sub> = V<sub>s</sub> + V<sub>Q</sub> (z-dependent)



#### **FM-KPFM**

#### Imaging ...

#### Doped nanocrystals inducing charge transfers to the substrate



topo : *A<sub>pp</sub>* = 20 *nm*, Δf = - 5 Hz ; 1,7 μm \* 1,7 μm; 512 \*512 pixels; tip-sample distance of 4-6 nm



FM-KPFM :  $f_{ac} \sim 300$ Hz;  $V_{ac} = 200$  mV



# Amplitude Modulation Kelvin Probe Force Microscopy (AM-KPFM)



#### **AM-KPFM**





regulating  $F_{\omega}$  to zero (i.e:  $A_{\omega}=0$ ) gives :  $V_{dc} = V_s + V_Q$  (z-dependent)



# Example of a single-pass (UHV) AM-KPFM mode 1/2





#### Imaging ...



topo :  $A_{pp} = 20 nm$ ,  $\Delta f = -5 Hz$ ; 1,7 µm \* 1,7 µm; 512 \*512 pixels; tip-sample distance of 4-6 nm



AM-KPFM :  $V_{ac}$  = 200 mV;  $V_{dc}$  = 2 V;  $\tau$  = 100 µs



#### Similar image as FM-KPFM

#### **AM-KPFM**

A [too] large variety of implementations ...

- $\blacktriangleright \omega$  can be chosen freely :
  - close to the cantilever resonance (increases the sensitivity by  $Q^{1/2}$ )
  - at a cantilever higher eigenmode (e.g.  $f_1$ =6.2  $f_0$ )
  - at low frequency or high frequency, but out of resonance
- in conjunction or separately from topography imaging (single-pass versus lift/linear modes)
- with feedback loop on ... or off.



#### **AM-KPFM versus FM-KPFM**




## Side-capacitance effects in AM- and FM-KPFM – 1/5



Nullification of the  $\omega$  force component (AM-KPFM)

 $dC'_{1}/dz V_{ac} (V_{dc}-V_{1}) + dC_{2}/dz V_{ac} (V_{dc}-V_{2})$  $+ dC_3/dz V_{ac} (V_{dc}-V_3) = 0$ 

 $V_{dc} = \frac{dC_{1}/dz \cdot V_{1} + dC_{2}/dz \cdot V_{2} + dC_{3}/dz \cdot V_{3}}{dC_{1}/dz + dC_{2}/dz + dC_{3}/dz}$ 

#### **KPFM** : averaging technique



H. O. Jacobs et al. JAP (1998)

## Side-capacitance effects in AM- and FM-KPFM - 2/5



- intrinsic averaging effects in AM and FM modes
- $dC_i/dz$  less 'peaked' at the tip than  $d^2C_i/dz^2$ : less resolution in AM modes



## Side-capacitance effects in AM- and FM-KPFM – 3/5





#### Both FM- and AM- modes are sensitive to side-capacitance effects at small size



Appl. Phys. Lett. 96 103119 (2010)

## Side-capacitance effects in AM- and FM-KPFM – 4/5





KCI islands on Au 111 (topo)



boundaries





U. Zerweck et al., Phys Rev B 71 125424 (2005)

## Side-capacitance effects in AM- and FM-KPFM – 5/5





KBr on InSb(001)

**FM-KPFM** measurements

#### convolution in FM mode for structures with smaller size than the tip apex

FIG. 1. (a) FM-KPFM topography and (b)  $\Delta$ CPD images of KBr islands grown on InSb(001) surface ( $f_0$ =111, 1 kHz,  $\Delta f$  = -17 Hz). The white arrows indicate the KBr islands, which are topographically not resolved from the substrate terrace.



F. Krok et al., Phys. Rev. B 77, 235427 (2008)

#### **AM-KPFM versus FM-KPFM**



Justification, if AM and FM modes are performed on the same resonance (Q) :

 $dC/dz \cdot \Delta V_{dcmin, AM} \cdot V_{ac, AM} = F_{min} \text{ (limited by thermal noise)}$  $d^{2}C/dz^{2} \cdot \Delta V_{dcmin, FM} \cdot V_{ac, FM} = F'_{min} \text{ (limited by thermal noise)}$ 

for the same 
$$V_{ac}$$
:  $\Delta V_{dcmin, FM} / \Delta V_{dcmin, AM} = \left[ \frac{dC}{dz} / \frac{d^2C}{dz^2} \right] \cdot \left[ F'_{min} / F_{min} \right]$   
 $z / |\alpha - 1|$   $\sqrt{2} / A$   
if  $\frac{d^2C}{dz^2}$  prop to  $z^{-\alpha}$   
(in air  $\alpha \sim 1.5$ )

#### **AM-KPFM versus FM-KPFM**



Justification, if AM and FM modes are performed on the same resonance (Q) :

 $dC/dz \cdot \Delta V_{dcmin, AM} \cdot V_{ac, AM} = F_{min} \text{ (limited by thermal noise)}$  $d^{2}C/dz^{2} \cdot \Delta V_{dcmin, FM} \cdot V_{ac, FM} = F'_{min} \text{ (limited by thermal noise)}$ 

for the same 
$$V_{ac}$$
:  $\Delta V_{dcmin, FM} / \Delta V_{dcmin, AM} = \frac{\sqrt{2}}{|\propto -1|} \frac{z}{A} > 1$ 

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### **AM-KPFM versus FM-KPFM**





topo :  $A_{pp} = 20 \text{ nm}, \Delta f = -5 \text{ Hz}$ ; 1,7 µm \* 1,7 µm; 512 \*512 pixels; tip-sample distance of 4-6 nm



 $\begin{array}{l} \mbox{AM-KPFM}: \mbox{V}_{ac} = 200 \mbox{ mV}; \mbox{ V}_{dc} \\ = 2 \mbox{ V}; \mbox{ } \tau = 100 \mbox{ } \mu s \end{array}$ 

FM-KPFM :  $f_{ac} \sim 50Hz$ ;  $V_{ac} = 200 \text{ mV}$ 

# Can we measure quantitatively a work function difference ? (ac-crosstalk issues – AM KPFM in air)



## **Practical operation principle**



projection angle necessary for the KFM feedback loop KFM "equation" : dC/dz.  $(V_{dc}-V_s)$ .  $V_{ac}$ .  $\cos(\phi_{1\omega}-\phi) = 0$ 

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## Practical operation principle ... with ac cross-talks



KFM "equation" dC/dz.  $(V_{dc}-V_s).V_{ac}.\cos(\phi_{1\omega}-\phi)$ +  $A_{ct}$  .  $V_{ac}$  .  $\cos(\phi_{ct} - \phi) = 0$  $V_{dc} = V_s + A_{ct} \cdot \cos(\phi_{ct} - \phi) / dC/dz \cos(\phi_{1\omega} - \phi)$ This term depends 888 - on  $\phi$  ("drive phase") - on  $\phi_{10}$  (excitation frequency) on z (via dC/dz)

In practice (Brüker) : photodiode + mechanical ac-cross-talks



### **Cross-talk suppression/compensation**



## **Cross-talk suppression/compensation**



### Conclusion

#### This was an introduction lecture on

- Electrostatic Force Microscopy (EFM)
  - spectroscopy of electrostatic forces
  - sensitivity and limits
- Kelvin Probe Force Microscopy (KPFM)
  - basic implementations
  - AM-KPFM vs FM-KPFM
  - quantitative work function measurement issues



## **Questions ?**



