High Resolution Quantitative Kelvin Probe Force Microscopy—Principles and Applications

**PeakForce KPFM**

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Outline

• KPFM Background

• A New Mode: PeakForce KPFM
  • Improved Spatial Resolution and Accuracy
  • Improved Repeatability
  • Compatible with Quantitative NanoMechanical property mapping (PF-QNM)

• Summary
Many Ways of Doing KPFM

FM and PeakForce scaling do not compete

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<th>AFM</th>
<th>Tapping</th>
<th>PeakForce</th>
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<td>AM</td>
<td>TP-AM</td>
<td>PeakForce KPFM-AM</td>
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<tr>
<td>FM</td>
<td>TP-FM</td>
<td>PeakForce KPFM</td>
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Both AM & FM KPFM improves with lower k

Tapping is limited to high k levers due to adhesive forces. PeakForce Tapping k is not.

*Except TP-FM, all are done in lift-mode.
Two Known KPFM Modes

FM Provides high resolution and accuracy

- **AM**
  - Amplitude-Modulation

- **FM**
  - Frequency-Modulation
    - Better spatial resolution
    - Better accuracy

KPFM measures the work function difference of tip/sample.

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**Physical Review B 2005, 71(12) 125424**
The probe body-cone and lever is an equal potential body.

Charges are only present on the surface (holds for any good conductor).

The conical body surface is a stack-up of rings, each ring contributes to the total electric field in proportion to their capacitance (assumption).
Cantilever Simulation
Contribution to AM and FM

\[ \Delta C_l = \varepsilon \frac{W \Delta L}{H + z} \frac{l}{L} \] (normalized to Tip end per deflection on force)

\[ C_{Lever} = \int_0^L \varepsilon \frac{W}{H + z} \frac{l}{L} dl = \frac{1}{2} \varepsilon \frac{WL}{H + z} \]

\[ -\frac{1}{2} \frac{\partial C_{Lever}}{\partial z} = \frac{1}{4} \varepsilon \frac{WL}{(H + z)^2} \approx \frac{1}{4} \varepsilon \frac{WL}{H^2} \]

SCM-PIT: \( W=30 \text{ um}, L=225 \text{ um}, H=10 \text{ um} \rightarrow 16.875\varepsilon \)

\[ 1 \frac{\partial^2 C_{Lever}}{\partial z^2} = \frac{1}{2} \varepsilon \frac{WL}{(H + z)^3} \approx \frac{1}{2} \varepsilon \frac{WL}{H^3} \]

SCM-PIT: \( W=30 \text{ um}, L=225 \text{ um}, H=10 \text{ um} \rightarrow 3.375\varepsilon / \text{um} \)
ΔCᵩ = ε ΔA/
d
= ε \frac{2πh \tan(\theta)}{h + z} \Delta h

Integration of capacitance from cone tip to height h.

Cᵩ = \int_{0}^{h} \frac{2\pi \varepsilon h \tan(\theta)}{h + z} \, dh
= 2\pi \varepsilon \tan(\theta) \left( \frac{h}{z} - \ln \frac{h + z}{z} \right)
Tip Cone Contribution in KPFM

FM gradient detection isolates contribution from tip

- **FM-KPFM:**
  - The foremost 0.3% of the tip cone accounts for half of the signal in.
  - FM can achieve a lateral resolution better than 50nm.

- **AM-KPFM**
  - The contribution from the tip cone never reaches 50%.
  - Its lateral resolution is dictated by the um-scale lever.

**Graph:**
- **Cone Contribution%**
- **Height Inclusion (h/H)%**

Based on SCM-PIT Geometry:
W=30um, L=225um, H=10um, Cone Angle=45
Force Gradient changes the effective spring constant.

For a simple driven harmonic oscillator:

\[ \omega = \sqrt{\frac{k}{m}} \]

Frequency shift caused by electric force gradient:

\[ \Delta \omega = \frac{\omega}{2k} \Delta k = \frac{\omega}{2k} \Delta \left( \frac{\partial F_{el}}{\partial z} \right) \]
PeakForce KPFM Retains FM-KPFM’s High Resolution

PeakForce KPFM-AM

PeakForce KPFM
PeakForce KPFM
High Resolution Example

Single Strand Carbon Nanotube (~2nm)
**PeakForce KPFM vs FM-AM**

FM detection advantage maintained

FM sees larger and more localized contrast leading to *better accuracy*. AM contrast smaller and more convoluted.

Work functions: Sn 4.42 eV; Pb 4.25 eV

Sn$_{60}$Pb$_{40}$ Alloy
PeakForce KPFM Offers
Simultaneous Mechanical Information

PS=PolyStyrene
LDPE=Low Density PolyEthylene

Height 100 nm
Modulus 10 MPa
Deformation 25 nm
Adhesion 5 nN

Potential 150 mV

PS
LDPE

8/22/2012
PeakForce KPFM vs TP-FM
No spring constant conflicts, yields superior mechanical data in PeakForce Tapping Mechanical Property Maps

PeakForce KPFM

TP-FM

Sn-Pb Alloy

240 mV

235 mV

PeakForce Adhesion

Tapping Phase
### Improve Repeatability
Through Tight Parameter Control and Probe Design

### Sources of Uncertainty

<table>
<thead>
<tr>
<th>Sources of Uncertainty</th>
<th>Bruker Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating Frequency</td>
<td>Tight parameter control (ScanAsyst-KPFM):</td>
</tr>
<tr>
<td>Tip-Sample Separation</td>
<td>• Thermal tune for resonance frequency</td>
</tr>
<tr>
<td></td>
<td>• Fixed oscillation amplitude</td>
</tr>
<tr>
<td></td>
<td>• Optimal phase setting</td>
</tr>
<tr>
<td>Tip work function change due to tip wear</td>
<td>Probe Design:</td>
</tr>
<tr>
<td>Electrochemical reaction under bias</td>
<td>• Single tip material</td>
</tr>
<tr>
<td></td>
<td>• Proprietary way to limit DC current flow</td>
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</table>
PeakForce KPFM Repeatability
5x improvement over traditional KPFM

<table>
<thead>
<tr>
<th></th>
<th>Average</th>
<th>Std Dev</th>
<th>Maximum</th>
<th>Minimum</th>
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</thead>
<tbody>
<tr>
<td>Au-Al</td>
<td>0.825</td>
<td>0.019</td>
<td>0.847</td>
<td>0.796</td>
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<tr>
<td>Au</td>
<td>0.639</td>
<td>0.018</td>
<td>0.617</td>
<td>0.670</td>
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<tr>
<td>Al</td>
<td>-0.185</td>
<td>0.020</td>
<td>-0.159</td>
<td>-0.222</td>
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</tbody>
</table>

9 KPFM Probes
Bruker AFM + MBraun Glovebox
- Integrated, Turnkey

Vibration Isolation Table

<1ppm $O_2/H_2O$

Sturdy Support
It Must Be Artifact-free to be quantitative
But sometimes, Artifact can be deceivingly beautiful.
PeakForce KPFM
Lift Mode Offers a Means to Avert Artifact

Brush Polymer
250 nm x 250 nm

Potential Map Changes with Lift Height

While small tip-sample distance is desirable for high spatial resolution, it is sometimes necessary for tip to completely clear surface to avoid artifacts due to tip-sample direct contact.
Artifacts
PeakForce-KPFM: can be identified and avoided with Tapping KPFM-FM: can be unavoidable sometimes

KPFM-FM (Tapping mode, single-pass)

PeakForce KPFM Lift Height Test

Lift-Height 35nm
Lift-Height 40nm
Solar Cell
MultiCrystal Si
Organic Photovoltaic Applications: PCBM Crystals on MDMO-PCBM Matrix

Particles are PCBM crystals on matrix of MDMO-PCBM blend, ITO substrate. Sample courtesy of Dr. Philippe Leclere, University of Mons.

Work function downshifts 535 mV under 300-sun illumination.
But Tapping Mode Requires:
- $k$ to be not too small
- $Q$ not to be too big

Tapping and KPFM scaling in conflict.

Peak Force Tapping Mode Allows Freedom to use:
- Smaller $k$ (10x or more)
- Big $Q$ (10x or more)

PeakForce Tapping and KPFM scaling aligned.
PeakForce KPFM - A New Way of doing KPFM.

- It retains the high spatial resolution and accuracy of FM-KPFM.
- It acquires high repeatability through tight parameter control and probe design.
- It leverages PeakForce QNM to give simultaneous mechanical and electrical information.
- It bears the promise to further enhance FM-KPFM sensitivity.

We have come to a point that we can begin to call KPFM Quantitative, and High Resolution (spatial).
## Work Function Table

<table>
<thead>
<tr>
<th>Element</th>
<th>eV</th>
<th>Element</th>
<th>eV</th>
<th>Element</th>
<th>eV</th>
<th>Element</th>
<th>eV</th>
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<tbody>
<tr>
<td>Ag</td>
<td>4.52 – 4.74</td>
<td>Al</td>
<td>4.06 – 4.26</td>
<td>As</td>
<td>3.75</td>
<td>Au</td>
<td>5.1 – 5.47</td>
<td>B</td>
<td>~4.45</td>
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<tr>
<td>Ba</td>
<td>2.52 – 2.7</td>
<td>Be</td>
<td>4.98</td>
<td>Bi</td>
<td>4.34</td>
<td>C</td>
<td>~5</td>
<td>Ca</td>
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<td>Cd</td>
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<td>Ce</td>
<td>2.9</td>
<td>Co</td>
<td>5</td>
<td>Cr</td>
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<td>Cs</td>
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<td>Cu</td>
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<td>Eu</td>
<td>2.5</td>
<td>Fe</td>
<td>4.67 – 4.81</td>
<td>Ga</td>
<td>4.32</td>
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<td>Hf</td>
<td>3.9</td>
<td>Hg</td>
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<td>Li</td>
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<td>Lu</td>
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<td>Mg</td>
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<td>Mn</td>
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<td>Mo</td>
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<td>Nb</td>
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<td>Ni</td>
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<tr>
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<td>Pb</td>
<td>4.25</td>
<td>Pd</td>
<td>5.22 – 5.6</td>
<td>Pt</td>
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<td>Rb</td>
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<td>Re</td>
<td>4.72</td>
<td>Rh</td>
<td>4.98</td>
<td>Ru</td>
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<td>Sb</td>
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<td>Sc</td>
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<tr>
<td>Se</td>
<td>5.9</td>
<td>Si</td>
<td>4.60 – 4.85</td>
<td>Sm</td>
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<td>4.42</td>
<td>Sr</td>
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<td>Yb</td>
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<td>Zn</td>
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<td>Zr</td>
<td>4.05</td>
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</tbody>
</table>
PeakForce KPFM-HV
Measuring High Voltage the Soft Way—Principle

\[ F_{el} = -\frac{\partial U}{\partial z} = -\frac{1}{2} \frac{\partial C}{\partial z} (\Delta V)^2 \]

\[ \Delta V = V_{DC} - \frac{\Delta \phi}{e} + V_{AC} \sin(\omega t) \]

\[ F_{el} = \]

\[ \frac{1}{2} \frac{\partial C}{\partial z} ((V_{DC} - \frac{\Delta \phi}{e})^2 + \frac{1}{2} V_{AC}^2) \quad \text{DC Term} \]

\[ + \frac{\partial C}{\partial z} (V_{DC} - \frac{\Delta \phi}{e}) V_{AC} \sin(\omega t) \quad \omega \text{ Term} \]

\[ + \frac{1}{4} \frac{\partial C}{\partial z} V_{AC}^2 \cos(2\omega t) \quad 2\omega \text{ Term} \]
PeakForce KPFM-HV
Electric Potential of Static Charge

PeakForce-HV modes measures up to 200 V electrostatic potential with <15% relative error.
Electrostatic Potential on PDMS
Summary

PeakForce KPFM-that
• is Quantitative:
  High Resolution (spatial)
  Accurate
  Repeatable

• gives simultaneous mechanical and electrical information.
• bears the promise to further enhance FM-KPFM sensitivity.

PeakForce KPFM-HV extends potential range beyond ±200V.