Introduction to the Kelvin Probe for High Resolution Work Function Measurements

Prof. Iain D. Baikie
CEO

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MRS Exhibit Hall

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Profile - Iain Baikie

PhD 1982-88 Univ Twente (The Netherlands)
*UHV KP study of Si and Ge surfaces*


*UHV KP study of Metal surfaces*

RGU, Aberdeen UK 1990, Prof. 1997

Joint Position MBL, Woods Hole, MA
Profile - KP Technology

Founded in 2000, located in Scotland
130 “Baikie” Kelvin probe systems worldwide
350-400 Consultancy Companies
16 representative worldwide
UK Queens Award 2008
Current Research

• High and Low Work Function Materials- ESA. MIT

• Solar Cells - ECN, ANU
  “Surface Photovoltage Monitoring in R2R Deposition of thin Si solar cells”, van Aken et al, 24th European Solar Energy Conference, Hamburg Sept 2009


• Bio-Kelvin Probe for medical applications- Harvard,MIT
  “In vivo Applications of the Bio-Kelvin Probe”
  NIH funded collaborative research project started Aug 2009

• Instrumentation Development- KP Technology
Technique Review

- Short History
- Fermi-Level Equilibrium
- Off Null Measurements
- Gold-Aluminum example
- Traditional SKP and AFM-KP
What is a Kelvin Probe?

Vibrating electrode device that:

• Probes the outermost layers of materials
• Is sensitive to the nature of the topmost atoms
  – (type, charge, geometry)
• Is one of the most sensitive surface analysis technique available
• Works in air, in vacuum and under some fluids
• Does all of the above without touching the surface
Kelvin’s Probe

- Was proposed 111 years ago in Scotland
- Does not measure temperature!
- Is based upon equilibrium of energy (charge)
- Didn’t vibrate - plates moved my hand
- Was used to study ‘Contact Electrification’ of Metals

Sir William Thomson - Lord Kelvin
1824-1907

www.kelvinprobe.com
Boston, Home of the Vibrating Probe

- Developed less than one mile from the Hynes Convention Centre, on the other side of the Charles River
- William A Zisman
- Vibrating Probe Published Rev. Sci. Instrum, 3,p367 (1932)
- MS MIT 1928
- PhD Harvard 1932
- Piano Wire vibrating in an air stream to move the plates

Dr William A Zisman
The 2010 ‘Baikie’ Kelvin Probe

• Non-contact, non-destructive vibrating capacitor device used to measure the work function of conducting materials or surface potential of semiconducting or insulating surfaces.

• The technique is extremely sensitive to the topmost layers of atoms or molecules, work function resolution of 1 - 3 meV.

• Unique ‘off-null’ measurement system also maintains average tip-sample separation to within 1 μm, tip to sample tracking
The Work Function

- The Work Function is usually described as being the ‘least amount of energy required to remove an electron from a surface atom to infinity or equivalently the vacuum level’.

- When a group of atoms or molecules are brought together to form a solid the highest occupied energy level, or fermi-level is termed the work function.

- The Kelvin probe measures the work function ‘indirectly’, i.e. via equilibrium not via extracting electrons.
When two or more materials are brought together the Fermi-levels equalize by a flow of electrons from the lower work function to the higher. Detecting these electrons is in essence the way all Kelvin Probe systems work.

(A) The electron energy level diagram for two conducting specimens, where $F_{\text{tip}}$ and $F_S$ are the work functions of the tip and sample, and $e_{\text{tip}}$ and $e_S$ represent their Fermi levels.
(B) An external electrical contact is made between the tip and the sample, $e_{\text{Tip}}$ and $e_s$ equalise and the resulting flow of charge produces a potential gradient, termed the contact potential $V_{\text{CPD}}$. The two surfaces become equally and oppositely charged.

(C) Inclusion of a variable "backing potential" $V_b$ in the external circuit, permits biasing of the tip or sample.

At the unique point when $V_b = -V_{\text{CPD}}$, a null output signal is obtained but this is a position of high noise.
Kelvin Probe Static Capacitance

- Plane Parallel Displacement
- Newton’s Fringing Fields
- Lever-arm sensing area changes

a) Plot of \( \ln(C2) \) vs. \( \ln(d0) \); (a) the ideal plane-parallel capacitor, (b) the calculated fringing field capacity, (c) measured data.

b) The percentage fraction deviation of (a) parallel plate and (b) measured data, from the calculated fringing capacity.

Experimental layout showing screen electrode. \( V_s \) is the screen potential, SP and VP, respectively, denote the statistic and vibrating plates, OS is the earthed outer screen.

Off Null Measurements

Vibrate the tip, AC Signal Produced

Vibrating Probe Tip

Section of Surface

Probe

Sample

Kelvin Probe signal changes over time

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On Null Measurements

Close to Balance (Null) poor Signal to Noise Ratio (S/N)

Traditional Kelvin circuit: the periodic changing Kelvin capacity $C_k(t)$ drives a current $i(t)$ through output resistor $R$. The contact potential difference in work function. $C'$ represents the total parallel capacitance, $d_0$ and $d_1$ the Kelvin capacitor means spacing and amplitude of oscillation respectively.

The effect of random noise signal on the cpd measurement: for signal heights less than ‘a’ noise terms predominate.

Off Null Measurements

Off-Null High Signal to Noise Ratio (S/N)

(a) Main measurement loop,
(b) Software filter operation

\[ V_{\text{ptp}} = (V_c + V_b) R_f G C_0 \omega \varepsilon \sin (\omega t + \varphi) \]

Sketch of the determination of Vc. The gradient is inversely proportional to the probe-sample distance


www.kelvinprobe.com
Effect of Spacing

As probe comes closer Harmonic Content Increases, $V_{ptp}$ rises

$V_s(ptp)$ output signal as a function of modulation index $\varepsilon$ (a) ideal parallel plate, (b) actual data and fringing field. Input parameters $V_0 = V$, $d_0 = 0.33\text{m}$, $R = 1\text{G}\Omega$, $C=370\text{pF}$, $f=35\text{Hz}$

Fourier Composition

Normalized $C_n$ Fourier coefficients of measured data as a function of $\omega$ for $\varepsilon = (a)0.1$ and (b) 0.9 ($\alpha$ and $\beta$ waveforms). Note the growth in harmonic content in the latter case.

PC houses the digital oscillator (which powers the voice coil actuator), data acquisition system and motorised (x,y,z) stage controller. The signal is derived from a low-noise, high-gain current to voltage (I/V) converter mounted close to the tip.

The 2010 Baikie System

KP Technology systems are at the 8th Generation

- **Highest work function resolution** 0.001-0.003V
- **Off null and height regulation features**
- **Full digital control of all Kelvin Probe parameters**
- **High signal levels, Very high rejection of driver talk over noise**
- **Excellent system stability and repeatability**
- **Change tip allow user selectable spatial resolution 2, 0.05 mm**

SKP5050 Advanced Scanning Kelvin Probe System
Gold / Aluminium Reference Sample

Tip Size: 2mm
Scanning Area: 10x16mm
Operator: I. Baikie
Microscopic Case - Metal Surfaces

Extraction of Electron

Pulling Electron put takes energy about 5Volts termed the Work Function

Electrical Flow

From high to low energy

Aluminium - Gold Layer

Aluminium - Gold Metal Scan

Probe Tip

Aluminium

Gold

Gold, nm

Probe Tip

Aluminium
AFM-KP

- null based
- potential imaging
- operating within 30 nm

Sommerhalter, Matthes, Jager-Waldau, Lux-Steiner, HMI, Berlin

www.kelvinprobe.com
Traditional and AFM Based Kelvin Probes

- Non-Contact, Non-Destructive Mode of Operation
- Images surface potential, surface charge distributions

**Specifications**

<table>
<thead>
<tr>
<th></th>
<th>Traditional</th>
<th>KP-AFM</th>
</tr>
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<tbody>
<tr>
<td>Detection</td>
<td>Null and Off Null</td>
<td>Null</td>
</tr>
<tr>
<td>Energy (meV)</td>
<td>1-3 meV (&lt;1 meV)</td>
<td>10-20</td>
</tr>
<tr>
<td>Lateral</td>
<td>50µm (200 nm)</td>
<td>&lt;50 nm</td>
</tr>
<tr>
<td>Perpendicular (nm)</td>
<td>40</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Sample</td>
<td>&lt;1mm to 50 cm</td>
<td>100nm-25 µm</td>
</tr>
<tr>
<td>Calibration</td>
<td>Yes on Gold</td>
<td>No</td>
</tr>
<tr>
<td>Repeat Area</td>
<td>Yes, Macroscopic</td>
<td>Probably Not</td>
</tr>
</tbody>
</table>
Application Examples

• Ambient Scanning Kelvin Probe
• UHV KP and ambient KP
• Surface Photovoltage- Solar Cells
• Absolute Kelvin Probe (Photoelectric Effect)
MEMS: Laser Modified Organic Film on Silicon

Tip Size: 50µm
Scanning Area: a) 1.6x0.8mm
  b) 2x1.5mm
Operator: I. Baikie
  (Large WF change)

a) SAM coating UV light modification

b) Double bonded Ic on wafer coating

www.kelvinprobe.com
Single Electron Transistor Device

Tip Size: 50μm
Scanning Area: 2x2mm
Operator: I. Baikie
(Large WF change)
Al, Au, Si
Silicon Wafer with Organic Mono-Layer

Tip Size: 2mm
Scanning Area: 12x12mm
Operator: I. Baikie
(Large WF change)

Pattern of monomolecular layer in Si
Corrosion of Steel

Local Anode Corrosion Sample + 30min 3%NaCl Submersion

Tip Size: 50μm
Scanning Area: 4.5x4.5mm
Operator: I. Baikie
Organic Film on ITO / Glass

Tip Size: 2mm
Scanning Area: 22x22mm
Operator: I. Baikie
(WF variance ± 12meV)

Non homogenous coverage
Polymer Elector Anode Testing
Fingerprint on Brass

Tip Size: 50μm
Scanning Area: 4x6mm
Operator: I. Baikie
Scanning Kelvin Probe with Relative Humidity Chamber

The Scanning Kelvin Probe with Relative Humidity Chamber provides an environment where the relative humidity and sample temperature can be controlled to 1% and 1 °C respectively.

SKP5050 + RHC020 Controlled Environment Kelvin Probe System

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The Ultrahigh Vacuum Kelvin Probe allows for single point measurements to be performed under UHV conditions.

- **Work Function resolution of 1 to 3 mV**
- **100% UHV compatible to 2x10^{-11} mBar**
- **CF 70 (2.75 inch) OD Mounting Flange**
- **User specified flange to sample spacing**
- **User specified Tip sizes**
- **50mm or 100mm Translator**
- **Manual/Motorised Options**
Sub-Atomic-scale layers

Example: Si(111) Oxidation

1. Oxygen

2. Surface of Silicon 1,000,000

3. 1 nm

4. Adsorbed Layers

www.kelvinprobe.com
UHV KP Si(111) + O2

UHV Work Function scan of Si(111)

Creation of dipole layer, +1000 meV

SPS depletion of surface states

www.kelvinprobe.com
Oxygen uptake curves on a clean Re surface as a function of stepwise temperature increments (300-800) K. The Re was cleaned between each adsorption. The clean Re work function is 5.1eV as 300 K.

UHV KP with STM

a) Shows the STM image corresponding to the change in wf gradient at 0.2ML

Collection of wf data by UHVKP allow surface reaction to be mapped out. There after selective interesting coverage for in-situ UHV-STM

Ref: Prof I. D. Baikie
Various High Work Function Metals

Work function as function of substrate temperature in oxygen ambient for W, Mo, Re, Pd and Pt


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mc-Si Solar Cell

Silver Finger ~ 2 mm

AR/Passivation Layer: SiO₂ or Si₃N₄

Emitter: N₀ ranges from 10¹⁰ - 10¹⁶ cm⁻³

Substrate: mc-Si, N_A = 10¹⁶ cm⁻³

Silver Finger 165 µm

60 nm

n-type

100 nm

p-type

270 µm

Grain Boundaries

Aluminium Rear Metalisation

WF sensitive to voltage across the bariered PN junction (Voc) and surface traps in the passivation/ emitter interface

Microphotograph of Si₃N₄ terminated Solar Cell

Associated dark work function topography of the same region

www.kelvinprobe.com
PN junction, energy steps at surface passivation and internal PN junction

Ref: Prof I. D. Baikie
Surface Photovoltage

DC Light Pulse

A: Voc and Surface Traps
B: Surface Traps Alone

FSE and BSE Coated, Defective, Light Pulse

SPV: change in work function with time after light pulse

Ref: Prof I. D. Baikie
Surface Photovoltage Spectroscopy
Kelvin Probe

The SPS030 provides a light source and Automatic Light Wavelength Selector, (with a wavelength range 400-700 nm), 500x500x500 Optical Enclosure, optical table top and AC and DC surface photovoltage measurements.

- **Light Source** - 150W DC Regulated Quartz Tungsten Halogen With Fibre Optic Illumination
- **Wavelength Range** 400 - 700 nm
- **Wavelength FWHM** 25-30 nm
- **Multiple Measurement modes:**
  - KP Trigger / Optical Trigger
Energy level diagrams of the Kelvin probe in photocurrent measurement mode as a function of $V_b$ with $\phi_{\text{tip}} > h\nu > \phi_S$: (a) no photoelectrons are collected at the tip, (b), the onset of the photocurrent is measured where $\phi_{\text{tip}} = h\nu + qV_b(\text{onset})$ and in (c) the saturation current where $V_b = -V_{\text{CPD}}$. $\epsilon_{\text{tip}}$ and $\epsilon_S$ refer to the Fermi levels of the tip and sample, respectively.

Schematic of UHV system with its associated peripherals and facilities


www.kelvinprobe.com
Absolute work function of KP Tip

<table>
<thead>
<tr>
<th>Hg line / nm</th>
<th>$E_{ph}$ / eV</th>
<th>$V_b$(onset) / V</th>
<th>$\phi_{tp}$ / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>253.7</td>
<td>4.86</td>
<td>$-0.192 \pm 0.007$</td>
<td>4.672</td>
</tr>
<tr>
<td>312.6</td>
<td>3.95</td>
<td>$0.714 \pm 0.010$</td>
<td>4.662</td>
</tr>
<tr>
<td>365</td>
<td>3.38</td>
<td>$1.335 \pm 0.067$</td>
<td>4.716</td>
</tr>
<tr>
<td>Average</td>
<td>/</td>
<td>/</td>
<td>4.683 ± 0.030</td>
</tr>
</tbody>
</table>

Use various emission levels to determine Tip wf with 30 meV

Summary

- The KP, SKP, UHV KP is a very useful tool
- Ambient quickly get information
- Very sensitive to surface changes
- Extension to SPV, SPS
- Compatible with other techniques

For further product information or to request a quote please visit: [www.kelvinprobe.com/quote](http://www.kelvinprobe.com/quote)
Further Reading

Prof. Iain D. Baikie References

- Work function study of rhenium oxidation using an ultra high vacuum scanning Kelvin probe
  Prof I. D. Baikie et al, J. App, Phys., Vol. 88, No. 7 1 Oct ‘00

- Analysis of stray capacitance in the Kelvin method

- Study of high- and low-work-function surfaces for hyperthermal surface ionization using an absolute Kelvin probe

- Noise and the Kelvin method

- Multitip scanning bio-Kelvin probe

- Low cost PC based scanning Kelvin probe

- UHV-compatible spectroscopic scanning Kelvin probe for surface analysis
  Prof I. D. Baikie et al, Surface Science 433-435 (’99) 249-253

- In situ work function study of oxidation and thin film growth on clean surfaces
  Prof I. D. Baikie et al, Surface Science 433-435 (’99) 770-774

- Utilisation of a micro-tip scanning Kelvin probe for non-invasive surface potential mapping of mc-Si solar cells

- A novel detection system for defects and chemical contamination in semiconductors based upon the Scanning Kelvin Probe
  Prof I. D. Baikie et al, Surface Science 433–435 (’99) 622–626
Further Reading

KP Technology Client References

SURFACE PHOTOVOLTAGE
• Surface photovoltage study of photogenerated charges in ZnO nanorods array grown on ITO

• Size- and orientation-dependent photovoltaic properties of ZnO nanorods

• Direct comparison of photoemission spectroscopy and in situ Kelvin probe work function measurements on indium tin oxide films
Beerbom, M., Lagel, B., Cascio, A., Doran, B. and Schlaf, R

CORROSION
• Influence of surface morphology on corrosion and electronic behavior
Li, W. and Li, D.

• Effects of the strain rate of prior deformation on the wear-corrosion synergy of carbon steel

• Variations of work function and corrosion behaviors of deformed copper surfaces

• Degradation of organic coatings in a corrosive environment: a study by scanning Kelvin probe and scanning acoustic microscope
Further Reading

KP Technology Client References

THIN FILMS

• “Plasma coating and surface modification of amorphous carbon for biomedical applications,”
Maguire, P. D., Okpalugo, T. I. T. and Ahmad, I. RECENT DEVELOPMENTS IN ADVANCED MATERIALS AND PROCESSES (518), 2006, pp. 477--484.

• Tribological, mechanical and electrochemical properties of nanocrystalline copper deposits produced by pulse electrodeposition
Tao, S. and Li, D NANOTECHNOLOGY (17:1), 2006, pp. 65 - 78.

• Transparent conducting coatings made by chemical nanotechnology processes
Aegerter, Al-Dahoudi, Solieman, Kavak, and Oliveira, MOLECULAR CRYSTALS AND LIQUID CRYSTALS (417), 2004, pp. 589 - 598.

WORK FUNCTION MEASUREMENT

• Induced increase in surface work function and surface energy of indium tin oxide-doped ZnO films by (NH4)(2)S-x treatment

• Influences of tensile strain and strain rate on the electron work function of metals and alloys

• Effects of dislocation on electron work function of metal surface

• Electron work function: A parameter sensitive to the adhesion behavior of crystallographic surfaces

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