Kelvin Probe: A Powerful technique for non-destructive surface and interface studies

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“When you can measure what you are speaking about, and express it in numbers, you know something about it; but when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind.”
Lord Kelvin
Several properties of the Surface are required for various applications:

- Surface Morphology - Microscopy
- Surface chemistry - XPS
- Surface Mechanical properties – nano-indentation
- Surface Electrical / Electronic properties - Surface Resistance and Kelvin Probe
The basic question:

How can I achieve a junction or an Ohmic contact for a Semiconductor Device

Is answered by the knowledge of Surface Work function

We have to distinguish between Surface work-function and Bulk Work-function

Bulk work function can be measured by Photoelectric effect and X-ray

The only technique to measure the Surface Work function is

Kelvin Probe: the non-contact and non-destructive technique
In this presentation, I shall try to answer

- **What is Kelvin probe**

- **Why Kelvin probe**

- **How Kelvin probe**
Kelvin Probe

- Interface probing
- Adhesion and Corrosion
- Photocatalytic activity
- Surface Defects and Morphology
- Bacterial and bio-films
- Organic and polymer films
- Bio-medical implants
- Mechanical and Tribology
What is Kelvin probe:

- A surface analytical technique to probe surface and interfaces of metals, Semiconductors

Why Kelvin Probe:

This is the only technique which will leave the surface / interface virgin even after the measurement

How to build a Kelvin Probe:

I shall explain: it is very simple
Surface Modification / Surface Engineering:

Surface is most important for many applications

- Electro-chromics
- bio- electrodes
- photocatalysis
- SERS

Most surfaces are active

For example, Copper and Silver form Multi valence Oxides.

An understanding of the Dynamics of a Surface is very Critical in Devices.

All of you are quite knowledgeable on Surface Engineering and Modification

SERS Detection of Single molecule
Most of the methods of surface analysis involve bombarding the surface with a form of radiation - electrons, photons, ions, neutrons and then analysing the emitted radiation - electrons, photons, ions, neutrons.

Surface analysis with high energy photons, electrons and ions affects the surface via desorption, dissociation, oxidation, localized diffusion and ionization.
Kelvin Probe Principle:

When metals of dissimilar work-function are electrically connected, electrons from higher work function metal flows into the metal with a lower work-function till thermodynamic equilibrium is established.
A Short History of The Kelvin Probe

- First described by Lord Kelvin in 1897 for the measurement of Volta potentials, contact potentials and/or surface potentials (for non-metals);
- Modified by Zisman in 1932 as a vibrating capacitor;
- Improved and developed over the years by many others
Kelvin Probe:

Principle of CPD Measurement of a metal (Semiconductor) – metal system

Kelvin probe measures the Contact Potential Difference (CPD) With a reference electrode.

CRC Press (2009)
ISBN : 1420080776
**Kelvin Probe and Contact Potential Difference**

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**Kelvin Probe and Contact Potential Difference**
When electrical contact is made, the flow of charge allows the Fermi levels to equalize, giving rise to a surface charge and potential difference, $V_c$ (or contact potential).
Kelvin Probe

Determining relative changes in work functions is done by measuring the work function difference between two materials.
The Basic Kelvin Probe

\[ i = (V_{CPD} + V_{DC}) \frac{dC}{dt} \]

\[ V_{dc} = -V_{CPD} \quad i_{ac} = 0 \]
The time varying capacitance is

\[ C(t) = \frac{\varepsilon_0 A}{d(t)} \]

\[ d(t) = d_0 - a \sin(\omega_0 t) \]

The current generated by the vibrating capacitor is

\[ i(t) = \frac{d}{dt} \left( (V_B - V)C(t) \right) \]

\[ i(t) = (V_B - V) \frac{d}{dt} \left( \frac{C_0}{1 - m \sin(\omega_0 t)} \right) \]
The discrete Fourier series expansion of \( i(t) \) can be written as

\[
i(t) = a_0 + \sum_{n=1}^{\infty} \left[ a_n \cos(n\omega_0 t) + b_n \sin(n\omega_0 t) \right]
\]

\[
a_0 = 0
\]

\[
a_n = \frac{(1+(-1)^{n+1})nm^{n-1}}{(1+\sqrt{1-m^2})^n \sqrt{1-m^2}} \left[ m\omega_0 C_0 (V_{CPD} - V_B) \right]
\]

\[
b_n = \frac{(1+(-1)^n)nm^{n-1}}{(1+\sqrt{1-m^2})^n \sqrt{1-m^2}} \left[ m\omega_0 C_0 (V_{CPD} - V_B) \right]
\]
Kelvin method of measuring CPD can be used for wider range of materials, temperatures and pressures than the other methods.

This technique does not run the risk of disturbing the surface, which is of vital importance in studying weakly bound adsorbates.

Kelvin probe-in principle is totally non-destructive
Scanning Kelvin probe

Stepper motor controlled X-Y stage

Spatial resolution - 10µm

Hemispherical probe tip (0.5 mm dia.) made of stainless steel
The Vibrating Kelvin probe (2013) Built at ARCI
Surface Photovoltage Spectroscopy (SPS)

Surface state depopulation

\[ e^- \quad h\nu \geq E_c - E_t \]

Surface state population

\[ e^- \quad h\nu \geq E_t - E_V \]

\[ E_C \quad E_F \quad E_V \]

\[ V_{S\text{ Dark}} \quad V_{S\text{ Light}} \]
Surface Photovoltage - SPV

Reference
Probe

n-type
Semiconductor

$\phi_{\text{Ref}}$

$E_F$

$E_C$

$E_V$

$hv > E_g$

$eV_{\text{CPD}}$

$e \Delta V_{\text{CPD}}$

$e |V_s|$

$e \Delta |V_s|$

$h\nu > E_g$
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

Aluminium - Gold

Electrical

From high to low energy

Aluminium  Gold  Platinum

Probe Tip

Aluminium  Gold

Probe Tip

Gold, nm
AFM-KP

- null based
- potential imaging
- operating within 30 nm

Sommerhalter, Matthes, Jager-Waldau, Lux-Steiner, HMI, Berlin
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>
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<tbody>
<tr>
<td>Detection</td>
<td>Null and Off</td>
<td>Null</td>
</tr>
<tr>
<td>Energy</td>
<td>Null 1-3 meV (&lt;1 meV)</td>
<td>10-2</td>
</tr>
<tr>
<td>(meV)</td>
<td>meV) 50μm (200 nm)</td>
<td>0</td>
</tr>
<tr>
<td>Lateral</td>
<td>40</td>
<td>&lt;50 nm</td>
</tr>
<tr>
<td>Perpendicular</td>
<td>&lt;1mm to 50 cm</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>(nm) Sample</td>
<td>Yes on Gold</td>
<td>100nm-25</td>
</tr>
<tr>
<td>Calibration Repeat Area</td>
<td>Yes, Macroscopic</td>
<td>μm No</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Probably Not</td>
</tr>
</tbody>
</table>

- Detection: Null and Off vs. Null
- Energy: Null 1-3 meV (<1 meV) vs. 10-2 meV
- Lateral: 50μm (200 nm) vs. <50 nm
- Perpendicular: <1mm to 50 cm vs. <1 μm
- Sample: Yes on Gold vs. 100nm-25 μm
- Calibration Repeat Area: Yes, Macroscopic vs. μm

Probably Not
Application Examples

- Ambient Scanning Kelvin Probe
- UHV KP and ambient KP
- Surface Photovoltage- Solar Cells
- Absolute Kelvin Probe (Photoelectric Effect)
CPD (with ambient oxygen) for a 200 nm Copper thin film as a function of time

Note the positive values of CPD on the y axis.
CPD (with ambient oxygen) for a 1000 nm Copper thin film as a function of time

Note the NEGATIVE values of CPD on the y axis.
Surface Photovoltage Spectroscopy (SPS)

Surface state depopulation

Surface state population

\[ h\nu \geq E_C - E_t \]

\[ V_S \text{ Dark} \]

\[ V_S \text{ Light} \]

\[ E_C \]

\[ E_F \]

\[ E_V \]
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
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

Pattern of monomolecular layer in Si

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

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 $2 \times 10^{-11}$ 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

UHVKP020: UHV Kelvin Probe
Sub-Atomic-scale layers

Example: Si(111) Oxidation
UHV KP Si(111) + O2

Creation of dipole layer,
+1000 meV

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 $\psi$ gradient at 0.2ML.

Collection of $\psi$ data by UHVKP allow surface reaction to be mapped out. Thereafter select 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

mc-Si Solar Cell

Silver Finger ~2 mm Silver Finger 165 µm

AR/Passivation Layer: SiO₂ or Si₃N₄ 60 nm

n-type Emitter: N_D ranges from 10²⁰ - 10¹⁸ cm⁻³ 100 nm

p-type Substrate: mc-Si, N_A = 10¹⁶ cm⁻³ 270 µm

Aluminium Rear Metalisation

WF sensitive to voltage across the barri ered 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
Solar Cell Energy Band Diagram

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

SPV: change in work function with time after light pulse

Ref: Prof I. D. Baikie
The Kelvin probe system in our Surface Lab has been extensively used to study various processes and phenomena based on the electron behavior of materials using the electron work function (EWF) as a fundamental parameter.
Surface photovoltage spectroscopy – an advanced method for characterization of semiconductor nanostructures

Article · January 2010

Kelvin probe and ultraviolet photoemission measurements of indium tin oxide work function: a comparison
Kelvin probe force microscopy and its application

Wilhelm Melitz\textsuperscript{a,b}, Jian Shen\textsuperscript{a,b}, Andrew C. Kummel\textsuperscript{a}, Sangyeob Lee\textsuperscript{a,*}
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
Amplitude (a.u.)

time (s)

m=25/30

B

D
\(a = 25 \, \mu\text{m}\)

\(f = 71.6 \, \text{Hz}\)

2F - mode

\(|V_{CPD}| \, (\text{mV})\)

\(d_0 \, (\mu\text{m})\)
The photoelectric work function refers to the removal of an electron possessing a particular energy in the metal.

True work function refers to the removal of an electron possessing an energy equal to an average value for true electron in the conduction band.
Principle of Photoemission spectroscopy
Ag on SiO$_2$

(Yield)$^{1/2}$ vs. Photon energy (eV)
n-type semiconductor
The diagram shows the relationship between SPV (mV) and Photon energy (eV) for different samples labeled (a) to (f). The curves indicate transitions at energies (E_v + 0.12) eV and (E_v + 0.45) eV.