

Ambient pressure photoemission spectroscopy of metal surfaces



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ABSTRACT

We describe a novel photoemission technique utilizing a traditional Kelvin probe as a detector of electrons/atmospheric ions ejected from metallic surfaces (Au, Ag, Cu, Fe, Ni, Ti, Zn, Al) illuminated by a deep ultra-violet (DUV) source under ambient pressure. To surmount the limitation of electron scattering in air the incident photon energy is rastered rather than applying a variable retarding electric field as is used with UPS. This arrangement can be applied in several operational modes: using the DUV source to determine the photoemission threshold (Φ) with 30–50 meV resolution and also the Kelvin probe, under dark conditions, to measure contact potential difference (CPD) between the Kelvin probe tip and the metallic sample with an accuracy of 1–3 meV. We have studied the relationship between the photoelectric threshold and CPD of metal surfaces cleaned in ambient conditions. Inclusion of a second spectroscopic visible source was used to confirm a semiconducting oxide, possibly Cu₂O, via surface photovoltage measurements with the KP. This dual detection system can be easily extended to controlled gas conditions, relative humidity control and sample heating/cooling.

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1. Introduction

The traditional Kelvin probe (KP) [1] equipped with a macroscopic tip is a versatile tool for measuring, in a non-contact fashion, exquisitely small differences in work function ($\Delta\Phi$, ΔE_f) or contact potential (CPD) between a vibrating metallic reference electrode and a metallic or semiconducting sample. Traditionally the Kelvin method has been applied for in-situ characterization of metals and semiconductors [2–5]. More recently it has been utilized in studies under ambient conditions of organic semiconductors: surface photovoltage characterization of bulk heterojunction organic solar cells [6]; *p*-type doping of P3HT with F₄TCNQ [7] and Φ -tuning of graphene [8] and ITO [9].

CPD is essentially a difference method, to calculate absolute sample Φ data assumptions are required on Φ_{tip} and its stability under experimental conditions. Both assumptions are potentially sources of experimental error. Baikie et al. [10] have described a UHV calibration method using a Hg lamp as a UV light source and a low- Φ sample in a retarding field configuration to the KP tip. Previous studies of metals [11] and ITO [12] have been performed using a combination of vacuum UPS measurements (absolute Φ) and CPD. However, these studies involve *separate* UHV

photoemission (PE) and ambient pressure CPD measurements. The underlying assumptions are (a) that ambient samples remain unaffected by the vacuum conditions and (b) samples generated in vacuum remain stable after exposure to ambient gases such as O₂ and H₂O.

In this paper we report, for the first time, a combination of ambient pressure photoemission spectroscopy and CPD using a 2 mm diameter Kelvin probe. In both measurements the *same tip electrode* is used as the current collector and the two measurements can be conducted quasi-simultaneously. An advantage of this new procedure is that Φ_{sample} is determined independent of Φ_{tip} .

This method can readily extended to semiconductor surfaces to include surface photovoltage spectroscopy (SPV), providing information on non-neutral surface space-charge regions (SCR) [13]. An advantage of this arrangement is that this arrangement technique can characterize Φ , E_f , and surface potential V_s , allowing monitoring of changes in energy barriers within electronic layers and devices as a function of exposure to ambient conditions, for instance diffusion of O₂, H₂O. The metals described in this study are in general use as anode/cathodes in solar cells or in the case of copper oxide as a photon absorber.

1.1. Experimental methods 1: CPD/SPV

The CPD generated by vibrating metallic tip in proximity to a dissimilar metal surface is equal to their difference in work function, i.e. $eV_{\text{CPD}} = e(\Phi_{\text{KP}} - \Phi_{\text{M}})$ see Fig. 1. When electrical contact is

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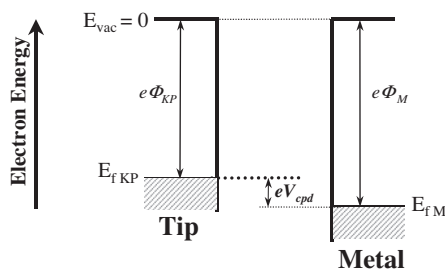


Fig. 1. Electron energy diagram for a metallic Kelvin probe tip of work function Φ_{KP} and dissimilar metal sample of work function Φ_M . The energy difference between the two Fermi-levels is equal to eV_{cpd} , i.e. $eV_{cpd} = (E_{fKP} - E_{fM})$. E_{vac} represents the vacuum level.

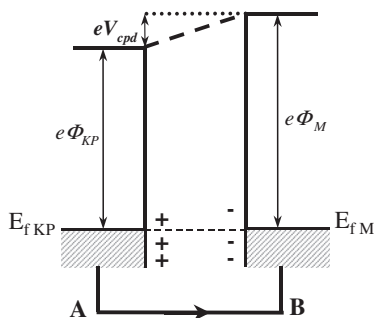


Fig. 2. Upon electrical contact the metal Fermi-levels equalize via a transfer of electrons from the lower work function tip to the metal sample. This results in a positively charged tip and a negatively charged sample and an associated electric field between the two adjacent surfaces. If an external emf, termed V_b is included between points A and B in Fig. 2, then the relative position of the metal sample Fermi-level can be altered. When the Kelvin probe tip is vibrated to produce a modulated capacity, then the peak-to-peak output V_{ptp} will be proportional to $(V_b - V_{cpd})$. At the unique point where, $V_b = V_{cpd}$ the surface charges disappear and the electric field between tip and sample is zero (or null).

made between the two metals charge flows from the lower work function to the higher, resulting in a negatively charged high work function surface and a positively charged low work function surface. An electric field now exists between the two metals, see Fig. 2. If an externally controlled emf, termed the backing potential V_b , is inserted between points A and B in Fig. 2, then the relative position of the metal sample Fermi-level can be altered. When the Kelvin probe tip is vibrated to produce a modulated capacity, then the peak-to-peak output V_{ptp} will be proportional to $(V_b - V_{cpd})$. At the unique point where, $V_b = V_{cpd}$ the surface charges disappear and the electric field between tip and sample is zero (or null).

Unfortunately the null position coincides with a minimum in the signal to noise (S/N) ratio, consequently all null-field Kelvin probes are liable to errors resulting from laboratory noise, stray capacity and overtalk from the probe vibration frequency and its harmonics. The off-null detection method described by Baikie [1] alleviates these issues by employing a current-sensitive approach preserving a high signal level. Further tip-to-sample capacity information can be used to minimize the environmental stray capacity effect and allow sub-micron tip-to-sample positioning. Fig. 3 illustrates this method: assuming the tip potential is changed from V_{b1} to V_{b2} then the output signal changes from V_{ptp1} to V_{ptp2} . The null position can be calculated with 1–3 meV resolution from two high signal level measurements and the gradient M of the $\Delta V_{ptp}/\Delta V_b$ line can be used in a feedback control loop to maintain a mean tip-to-sample distance aiding initial approach, repeatability and scanning.

The Kelvin probe used in this study utilizes a 2.0 mm diameter tip with a gold alloy coating. It was operated at 70 Hz and the tip-to-sample mean spacing was approximately 1.0 mm with a PTP vibration amplitude of 0.460 mm. The Kelvin probe is located in a Faraday cage allowing the sample illumination to be controlled.

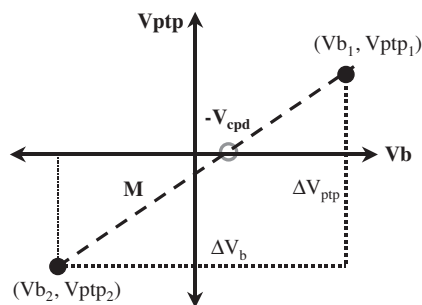


Fig. 3. If the tip is now vibrated then the peak-to-peak height of the resulting waveform is proportional to $(V_{cpd} - V_b)$ and the grey circle above represents the balance position. The minimum S/N ratio at null can be avoided by making two or more (V_{ptp}, V_b) measurements and then extrapolating. The gradient M of the extrapolated line is proportional to the fractional capacity [1] and can be used in a feedback circuit to maintain the tip-to-sample mean spacing.

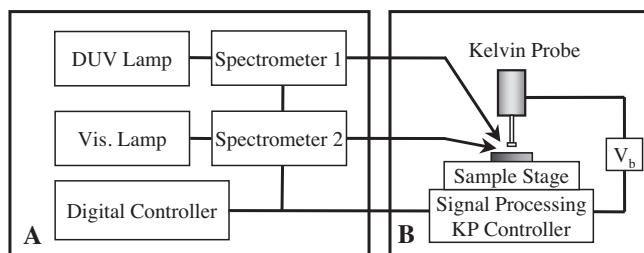


Fig. 4. Schematic diagram of the ambient photoemission spectroscopy system: (A) DUV lamp (D_2), motorized spectrometer and DUV optical filter arrangement produce a tuneable 3.0–7.0 eV beam. The DUV spectrometer enclosure is filled with N_2 to eliminate ozone production. The QTH lamp and visible spectrometer is used for surface photovoltage measurements. (B) Faraday Cage/Light Chamber with vertically mounted Kelvin probe which is used as a current detection in both photoemission and CPD measurement modes. V_b is the tip bias potential. The sample is mounted on a 3-axis stage with optional heater/cooler. The chamber can optionally be relative humidity controlled.

The sample was located on a motorized (x,y,z) sample stage with transitional position control <300 nm.

A second optical source, using a quartz Tungsten–Halogen lamp and associated spectrometer, permits sample illumination with either controllable intense white light or variable wavelength 400–1000 nm (E_{ph} : 3.1–1.24 eV) irradiation. This system can be used to test for formation of a semiconducting surface via changes in surface potential V_s due to illumination by a intensity modulated white light source or by scanning the wavelength above and below the band-gap energy E_g [13].

1.2. Experimental methods 2: Ambient pressure photoemission spectroscopy

The ambient pressure photoemission system comprises a deuterium (D_2) source coupled with a motorized grating monochromator. The sample is illuminated via a DUV optical fibre resulting in an elliptical surface profile of approx. 3×4 mm. Nitrogen gas is used to suppress the production of ozone in the DUV spectrometer. The range of incident E_{ph} is typically 3.0–7.0 eV, see Fig. 4. The photoelectron emission and ion-current detection process is a 4-step process, illustrated in Fig. 5:

1. DUV photons are absorbed within the metal surface region. Provided $E_{ph} \geq \phi_m$ electrons within the range of the inelastic electron mean free path (escape depth) of electron excitation can be emitted. The electron escape depth as a function of electron energy describes a U-shaped curve with a minimum depth of circa 0.5 nm between 50–100 eV [14]. In our case, with photon

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