

Quantifying Work Function using Kelvin Probe Systems

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Abstract: Quantifying the work function of materials is a major component of research dedicated to developing *in vacuo* electrical devices with high current density at low operating temperatures. These devices are regularly composites of more than one material and understanding the roles that the individual components play in determining the overall work function is at the frontier of this research [1]. The work function characterization technique outlined here is analysis using a Kelvin Probe System, which yields the opportunity to quantify a material's work function through measuring contact potential difference (CPD) or through surface photovoltage spectroscopy (SPS). In this paper, these separate techniques are outlined and experimental data is given for W and Ba, two elements of interest in device development.

Keywords: kelvin probe; work function; contact potential difference; surface photovoltage spectroscopy;

Introduction

The standard Kelvin Probe (KP) is a non-contact device for measuring the contact potential difference (CPD) between two metals. Specifically, it records the CPD between the metallic probe tip and the sample under inspection. This value is equivalent to the difference between the work function of the two metals:

$$\Phi_{\text{sample}} - \Phi_{\text{tip}} = \text{CPD (eV)}$$

where given a known work function of the tip, Φ_{tip} , and the measured CPD (in units of energy), the work function of the sample, Φ_{sample} , can easily be determined.

Contact Potential Difference: The Kelvin Probe is able to measure the CPD between the probe tip and the sample under inspection by using a parallel plate capacitor configuration between the two metals. Before coming into electrical contact with each other, two metals with different work functions are assumed to have different Fermi Energies. In fact, one way of visualizing the work function is the difference between a material's Fermi Energy and the energy of the vacuum, i.e. the energy it would take to move a surface electron to a point in space where it could have 0 kinetic energy and an equivalent 0 potential energy. See Figure 1. But when these two materials are brought into electrical contact with one another, electrons will transfer from the lower work function material to the higher work function material and their Fermi levels will equalize. This will also result in the lower work function material becoming positively charged and the higher work function

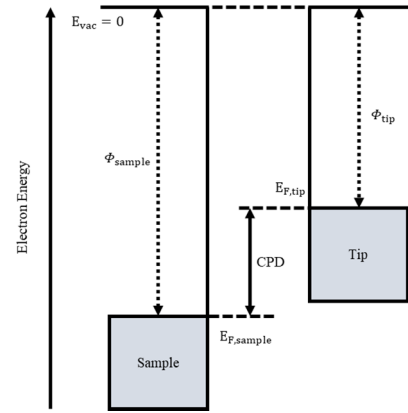


Figure 1. Energy diagram showing the difference between the work functions of the of the Kelvin Probe tip and the sample under inspection. E_{vac} is the vacuum level. (Adapted from ref. [3].)

material becoming negatively charged. An external emf, or backing potential, can then be gradually applied to the two metals until the surface charge between them disappears. The value of this baking potential, V_b , that balances out the charge on the plates is equal to the CPD between the

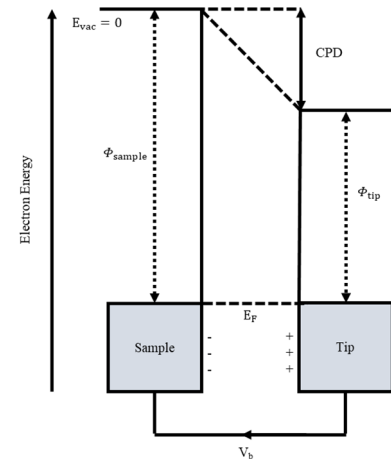


Figure 2. When two metals are brought into electrical contact, their Fermi Energies equalize. An externally applied field, V_b , is applied between them until the surface charges disappear. This value is equivalent to the CPD. (Adapted from ref. [3].)

metals. See Figure 2. A computer-integrated method of using this technique, which also significantly reduces the signal to noise (S/N) ratio measured by an oscillating Kelvin Probe, was developed by Baikie and Estrup [2] and is the basis of the CPD measurements made here.

Surface Photovoltage Spectroscopy: In this second technique, described by Baikie et al. [3], the sample under inspection is illuminated by a quartz Tungsten-Halogen lamp and associated spectrometer that allow the sample to be irradiated by light of 400 – 1000 nm wavelength. The photoelectrons ejected from the surface can be received by the Kelvin Probe and the sample's light response is measured as a function of incoming light wavelength. It is important to note the distinction, however, that measuring the photoemission threshold in metals yields the Fermi level and therefore work function, whereas measurements of the threshold emission for semi-conductors yields information on the band gap energy and ionization potential (because the ejected electrons in this case come from the semi-conductor's valence band). The work function can be readily extrapolated from a graph of the square root of photoemission vs incoming photon energy for metals or by using the cube root of photoemission vs photon energy for semi-conductors. This is in accordance with analysis done by Fowler [4], who outlined the relationship between photoemission spectra and the work function.

Results

Using the techniques described, we have been able to record the work functions of surfaces within a precision of less than 0.01 eV.

Contact Potential Difference: Using this technique, the following values of CPD were measured using an Au-plated, 2 mm diameter stainless steel Kelvin Probe tip and an unused W sputtering target specimen. See Figure 3 for the measurement results across six separate measurements.

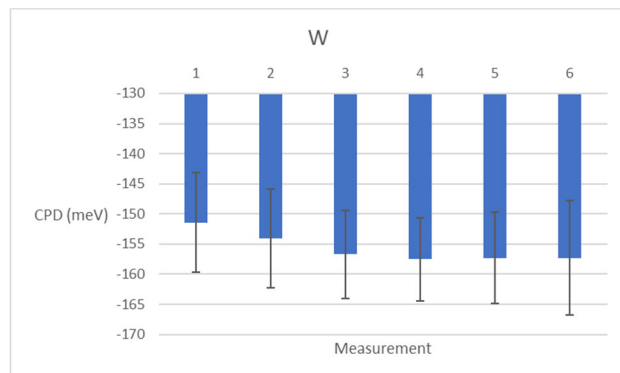


Figure 3. Six successive measurements of CPD between a gold Kelvin Probe tip and a tungsten sputtering target sample.

The average CPD measured here was -0.1557 eV with a standard deviation of 0.008 eV. From this average CPD value, the difference in work function equation presented in the introduction of this paper can then be used to obtain a calculated work function of 4.578 eV. The work function of the tip, 4.734 eV, had been previously obtained through measurements on known samples. This value is in near agreement with previously reported values of weighted work functions for tungsten. Given that the measurement was made in ambient conditions, the presence of oxygen on the tungsten surface cannot be neglected.

Additional Work

The remainder of this paper will explore CPD measurement results on barium, as well as results and calculations of the work function of tungsten and barium through the surface photovoltage spectroscopy technique outlined in the introduction. As well as a discussion in lieu of comprehending the ways that their different work functions interact when the materials are combined.

Summary

Understanding the electrical properties of these independent materials is vital to understanding their electrical properties when they are combined. Surfaces with lower work functions mean *in vacuo* electronic devices with higher current densities at lower operating temperatures can be produced. The two Kelvin Probe-based techniques outlined here, CPD measurement and SPS, provide an accurate and precise path to understanding surface work functions.

Acknowledgements

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References

1. Kirkwood, David M., et al. "Frontiers in thermionic cathode research." *IEEE Transactions on Electron Devices* 65.6 (2018): 2061-2071.
2. Baikie, I. D., and P. J. Estrup. "Low cost PC based scanning Kelvin probe." *Review of scientific instruments* 69.11 (1998): 3902-3907.
3. Baikie, Iain D., et al. "Ambient pressure photoemission spectroscopy of metal surfaces." *Applied Surface Science* 323 (2014): 45-53.
4. Fowler, Ralph H. "The analysis of photoelectric sensitivity curves for clean metals at various temperatures." *Physical review* 38.1 (1931): 45.