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Improving Kelvin probe work function measurement reliability

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Org. 1819: Material Characterization and Performance

U.S. DEPARTMENT OF ENERGY

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Work function in different materials

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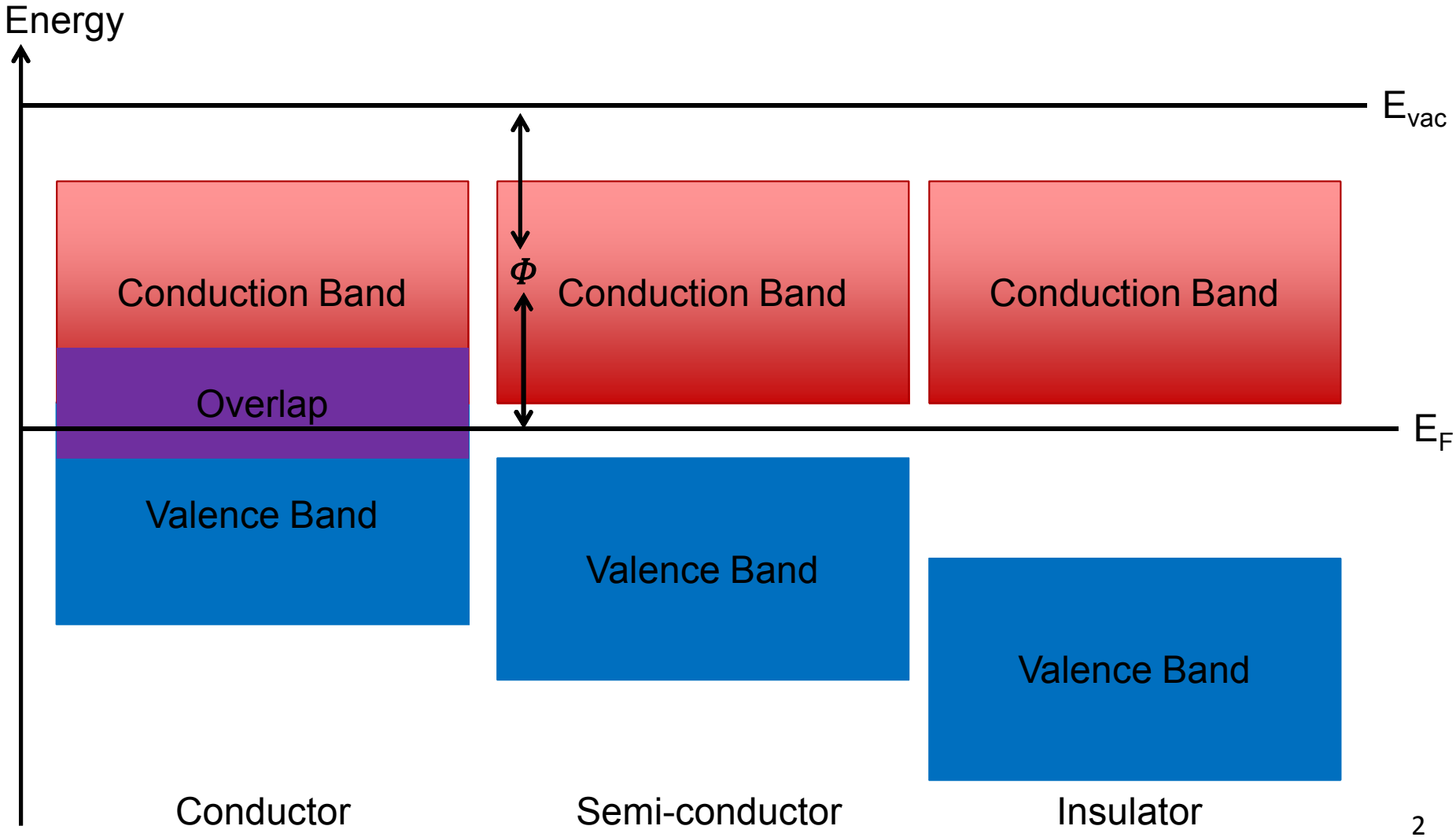
Work function (Φ) is the energy required to remove electrons from a material.



Work Function Measurement via Scanning Kelvin Probe

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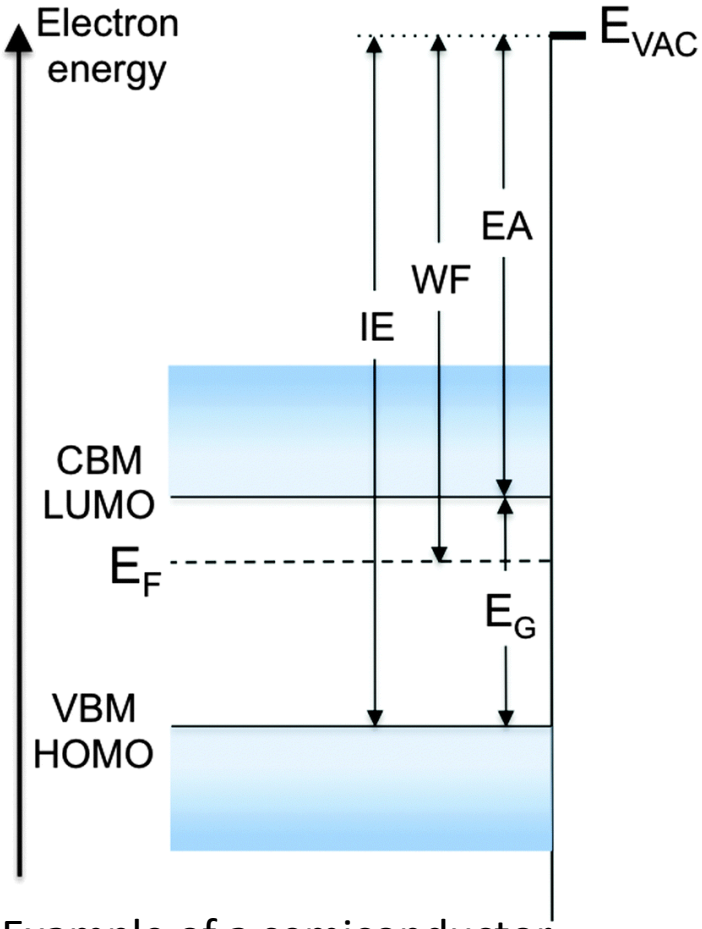
Photoelectric Effect:

- Light incident upon a metal surface may remove electrons from the metal if the light has a high enough frequency.
  - $K_{max} = h\nu - \Phi$ (Equation 1)

Contact Potential Difference (CPD):

- Potential difference between reference electrode (probe) and sample surface.
- Kelvin Probe measures the CPD electrically, from which the work function can be calculated.



Example of a semiconductor energy diagram[1].

Work Function Measurement via Scanning Kelvin Probe (SKP)

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$$C_K(t) = \frac{C_0}{1+\frac{d_1}{d_0}\sin(\omega t)} \text{(Equation 2)}$$

$$V_{ptp} = (V_c + V_b)R_f G C_0 \omega \frac{d_1}{d_0}\sin(\omega t + \varphi) \text{ (Equation 3)}$$

$$WF_{tip} = WF_{material} - CPD \text{ (Equation 4)}$$

$$WF_{sample} = WF_{tip} + CPD \text{ (Equation 5)}$$

The capacitance between the tip and sample is measured (Equation 2). From this capacitance, the peak-to-peak voltage of the system governed by Equation 3 can be used to calculate V_c (CPD). Standard materials with known work functions can be used to determine the work function of the tip (Equation 4), and the work function of the tip can be used to calculate the work function of the sample (Equation 5).

Work Function Measurement via Ultraviolet Photoelectron Spectroscopy (UPS)

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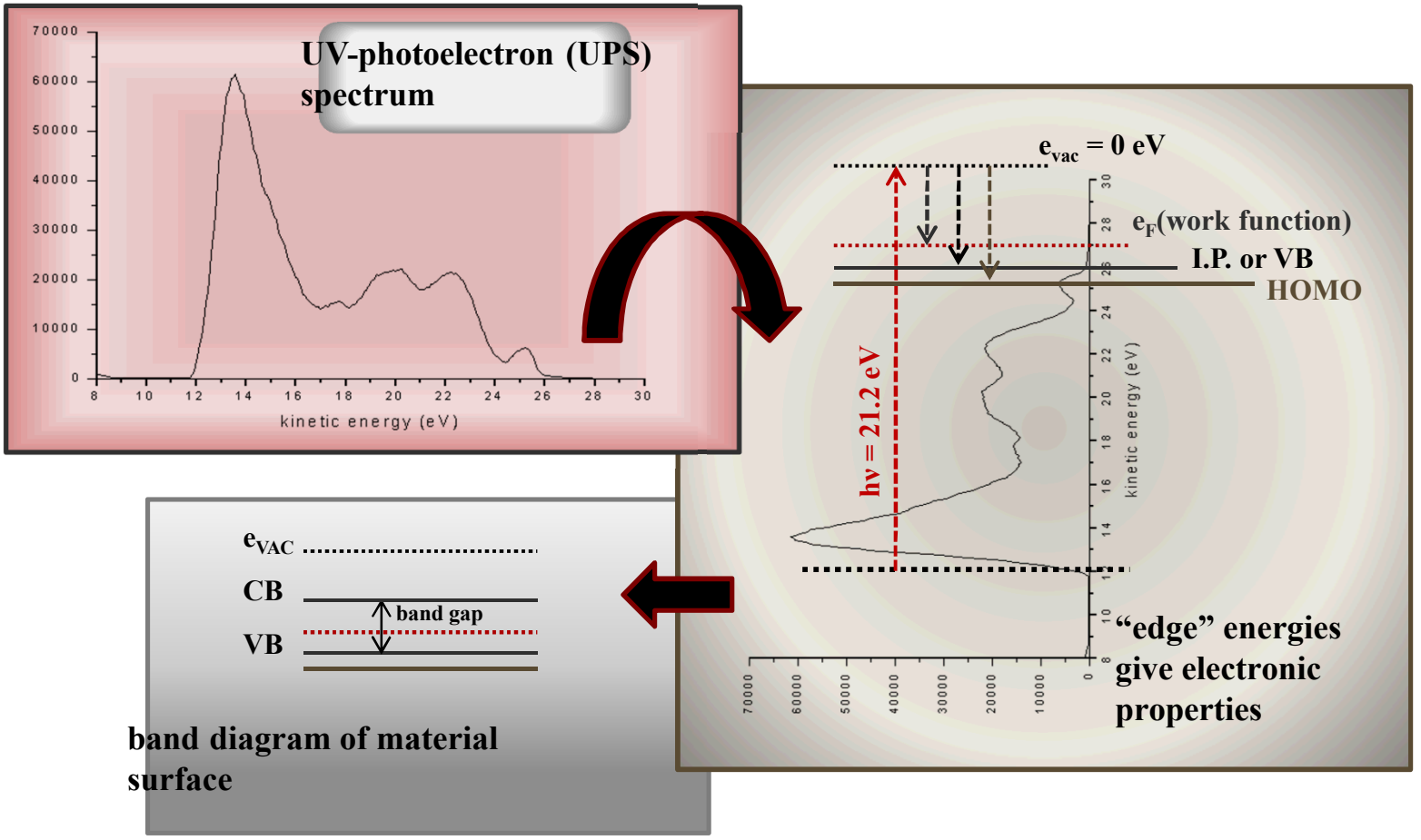
Photoelectric Effect:

- Light incident upon a metal surface may remove electrons from the metal if the light has a high enough frequency.
  - $B.E. = h\nu - (K.E. + \Phi)$ (Equation 6)
- Work function (Φ) is the energy required to remove electrons from a material.
- B.E. is the binding energy of the electron.
- K.E. is the measured kinetic energy of the emitted photoelectron.
- $h\nu$ is the energy of the ultraviolet photon source.

Work Function Measurement via Ultraviolet Photoelectron Spectroscopy (UPS)



Pros and Cons of SKP

Pros:

- Faster measurement time compared to UPS.
- Operates under ambient conditions.
- More sensitive to **bulk material.**

Cons:

- Less surface sensitive than UPS.
- Indirect **electrical measurement** of work function.

Images of enclosed SKP and the probe tip[3].

Calibration

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Using Equations 5 and standard work function values for carbon and gold, the work function of the gold probe tip is calculated on a daily basis.

Work Function of Au	CPD Au	Deviation	**Calculated WF of Tip (Au)**	Deviation	**Average WF of Tip (Au)**
5.1	27.7	4.8	5.0723	4.8E-03	5.066
5.1	39.1	5.9	5.0609	5.9E-03	
5.1	35.8	5.7	5.0642	5.7E-03	
Work Function of C	CPD C	Deviation	**Calculated WF of Tip(C)**	Deviation	**Average WF of Tip (C)**
4.81	-207.1	7.2	5.0171	7.2E-03	5.0178
4.81	-210	7.6	5.0200	7.6E-03	
4.81	-206.2	6.5	5.0162	6.5E-03	

Work Function of Tip	Standard Deviation	**Average WF of Tip**	Average STDEV of Tip
5.0447	3.903E-02	5.0418	2.5290E-03
5.04045	2.892E-02		
5.0402	3.394E-02		

Table of calculated work function for the probe tip over several days.

Work Function Calculation

Calculated Tip Values		
Date:	Tip WF (mV)	STDEV
06/22/2016	5.04	2.53E-03
06/23/2016	5.03	4.90E-03
06/24/2016	4.98	2.14E-03

After calibration, the tip work functions are used in calculating sample work functions.

Due to heterogeneity of surfaces, CPD measurements are averaged across samples.

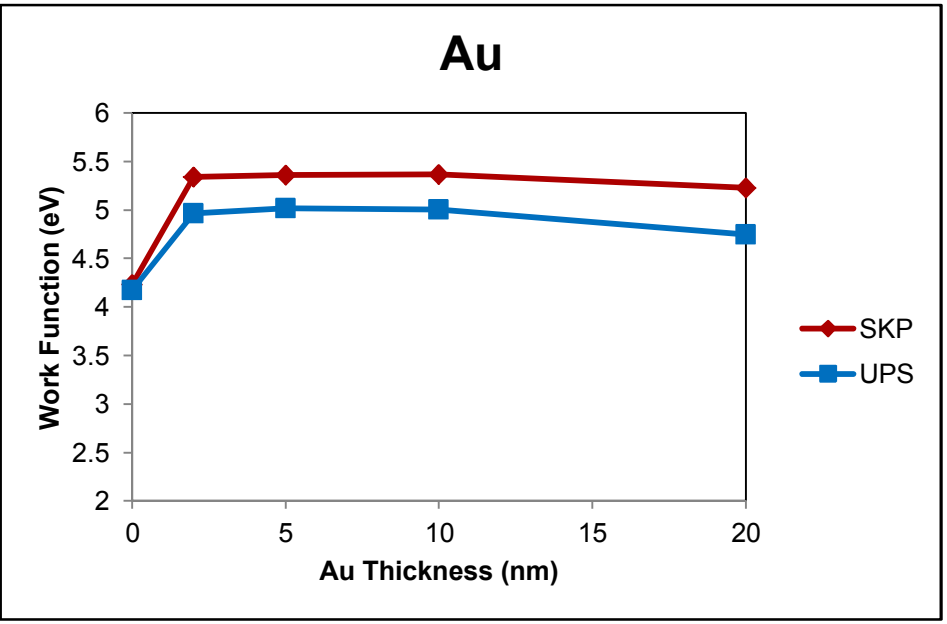
Weekly average work functions are the mean values of the average work functions values obtained each day of the week.

Work Function of Al film of varying thickness						
Date	Thickness (nm)	Area	CPD (mV)	STDEV	WF (eV)	STDEV
06/22/2016	0.5	1	-1256.8	6.2	3.7850	8.7290E-03
			-1247.1	6.5	3.7947	9.0290E-03
			-1242.0	6.3	3.7998	8.8290E-03
		2	-1289.6	6.7	3.7522	9.2290E-03
			-1309.1	7	3.7327	9.5290E-03
			-1301.0	6.8	3.7408	9.3290E-03

AVG WF(eV)	STDEV for Area	Average Work Function (eV)	Standard Deviation	Weekly Average WF (eV)	Weekly Standard Deviation
3.7931	7.5182E-03	3.7675	2.9146E-02	3.8187	6.2370E-02
3.7419	9.7964E-03				

UPS vs. SKP

UPS and SKP can potentially produce different work function values. However, similar trends appear in data from both methods.



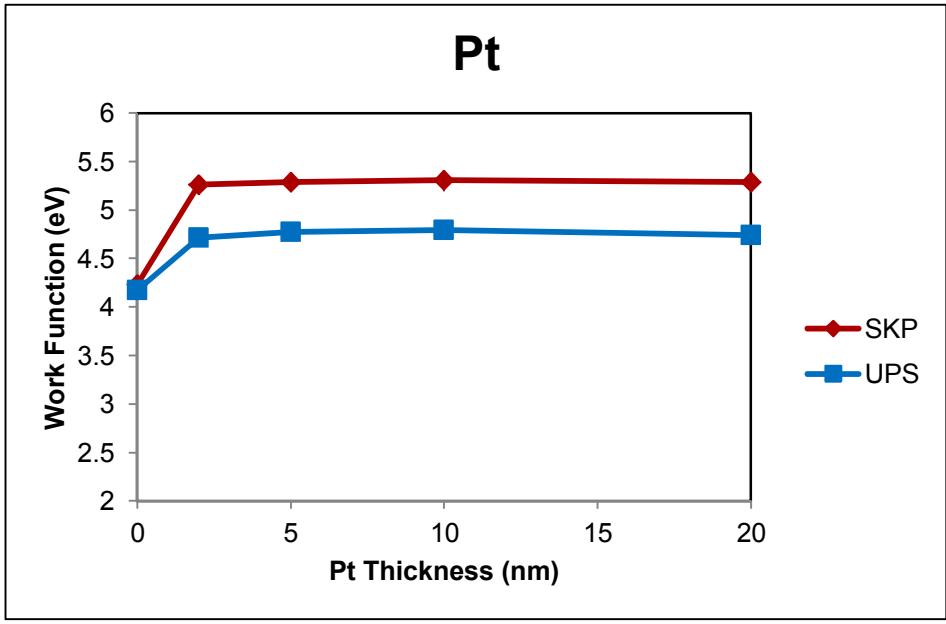
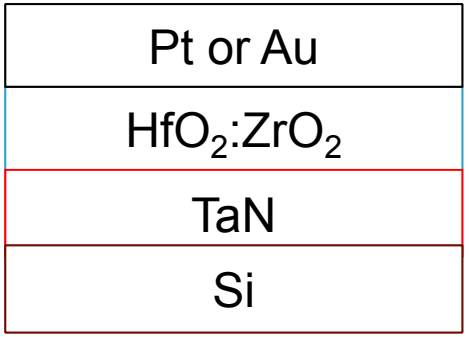
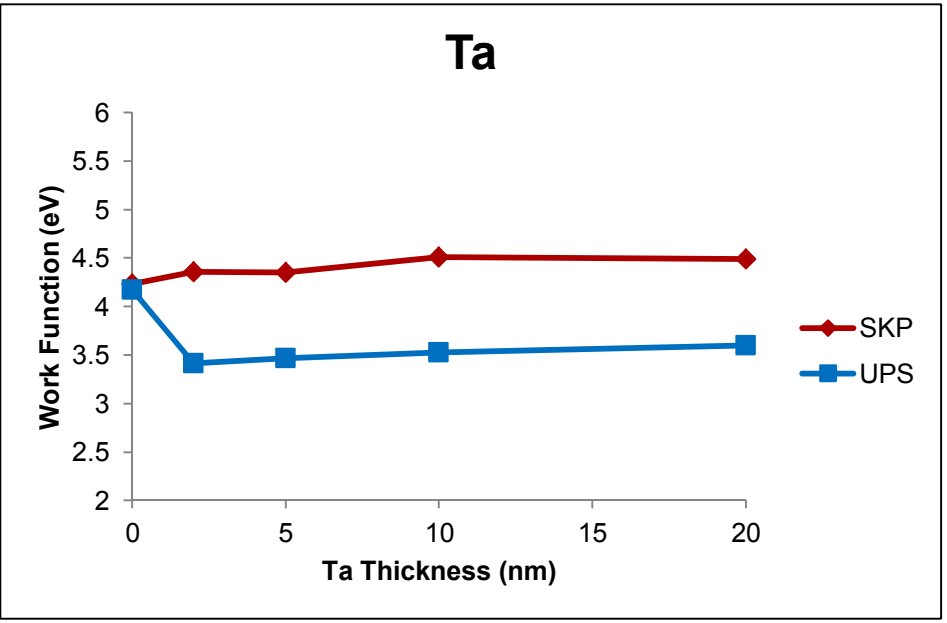


Illustration of the above materials (left). Pt and Au are noble metals that do not form oxide layers. The inclusion of any amount of Au or Pt increases the work function, and varying their thickness did little to change the work function.



UPS vs. SKP



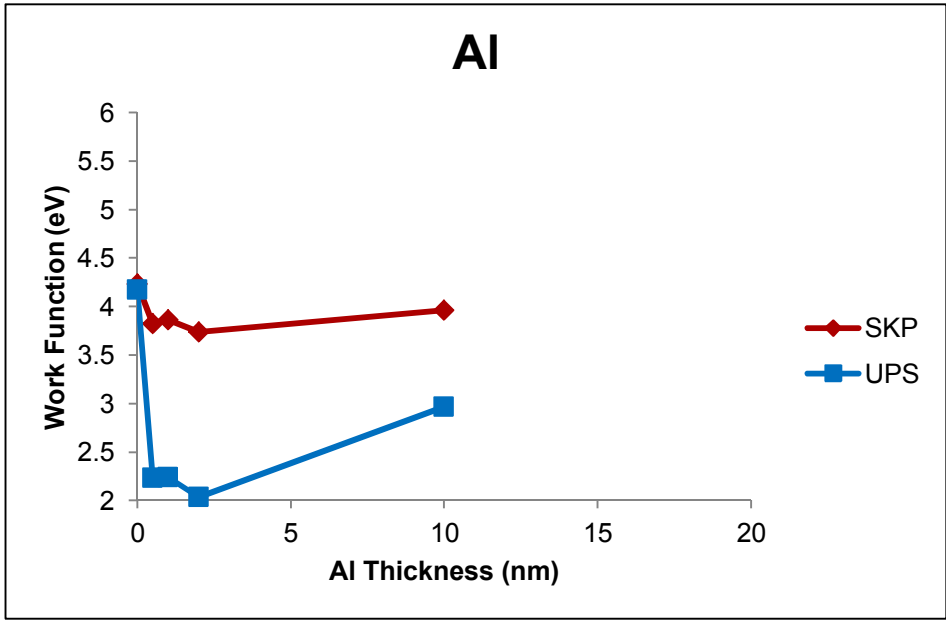
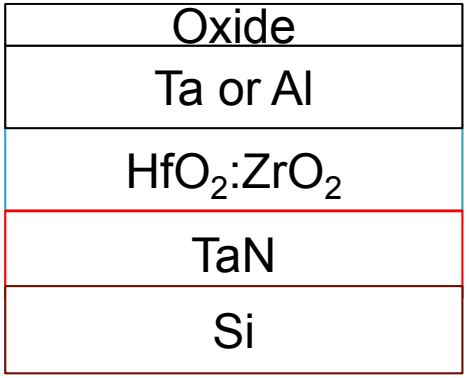
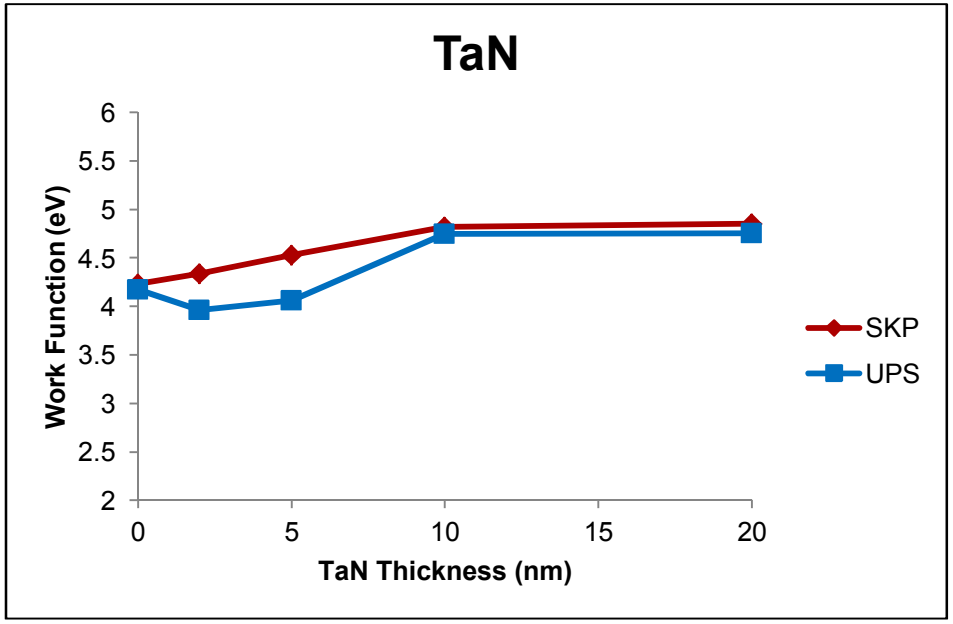
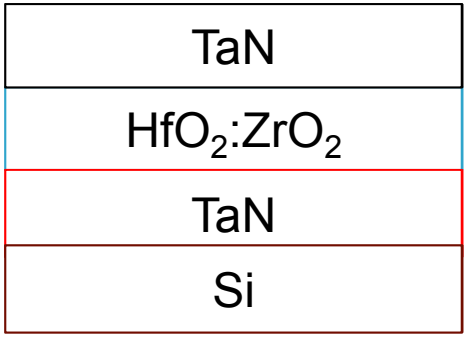


Illustration of the above materials (left). Al and Ta both form oxide layers readily. Upon inclusion of Ta or Al, the work function drops significantly.



UPS vs. SKP





TaN sits on the top of the same substrate as the previously mentioned materials.

Conclusions

- The deviation in work function measurements is **material dependent** for both SKP and UPS.
  - Generally, more conductive samples provide more reliable work functions.
- **Homogeneous materials** are easier to obtain useful work function data than **heterogeneous materials**.
- UPS is a more reliable method because it is a **direct measurement** of emitted photoelectrons.
  - However, contaminants can effect measurements because UPS is surface sensitive than SKP.
- As mentioned above, UPS measurements are made under **more inert environment** than SKP.
- Sample and/or probe tip **contamination** may measurably effect results.
  - e.g. graphite standard can contaminate the gold probe tip

References

1. Antoine Kahn, Fermi level, work function and vacuum level. *Matter. Horiz.,* **3**, 7010 (2016).

2. *Scanning Kelvin Probe User Manual* (KP Technology Ltd, Wick, Caithness, UK).
3. *www.kelvinprobe.com*