Exceptional service in the national interest

SAND2017-11810C

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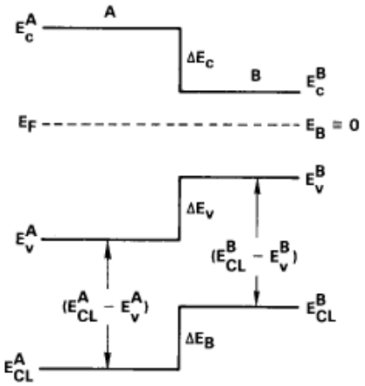

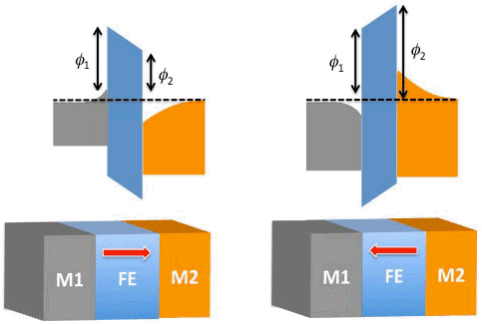

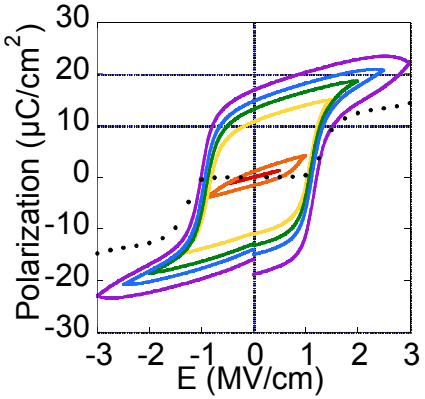

Quantifying Valence Band Offsets at Metal/(Hf,Zr)O_2 Interfaces for Ferroelectric Devices

MICHAEL BRUMBACH, SEAN SMITH, MICHAEL HENRY, JERAMY DICKERSON, JON IHLEFELD

AVS 64th International Symposium and Exhibition, Tampa, Florida, Oct. 29-Nov. 3, 2017

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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Band-diagrams…
What is Valence Band Offset?
Why do they matter?

Measurement of semiconductor heterojunction band discontinuities by x-ray photoemission spectroscopy

J. R. Waldrop, R. W. Grant, S. P. Kowalczyk, and E. A. Kraut

Citation: Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films **3**, 835 (1985); doi: 10.1116/1.573326

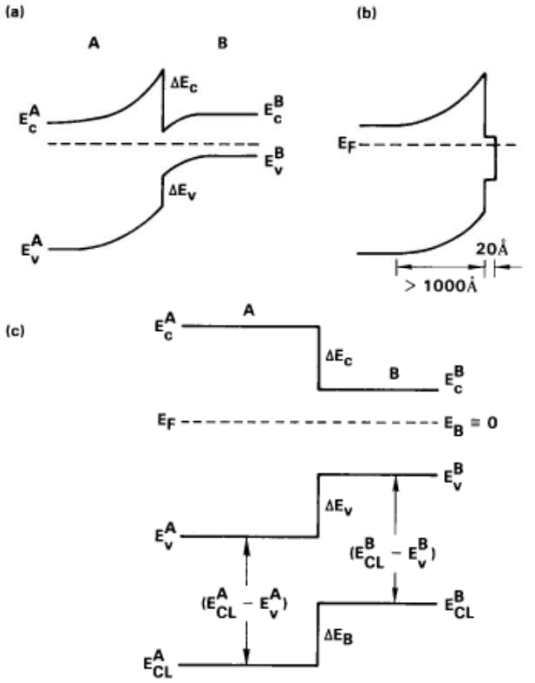
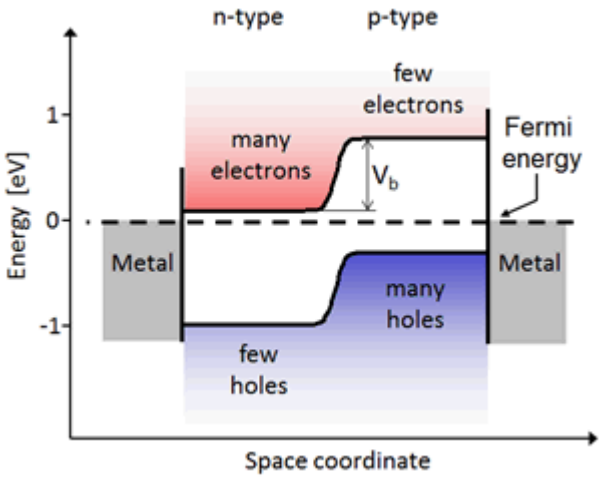


FIG. 1. (a) Typical "buried" heterojunction, (b) "exposed" thin heterojunction accessible to XPS analysis, and (c) schematic energy band diagram of thin, abrupt heterojunction interface.

Device performance is dependent on energy level alignments.



https://www2.pvlighthouse.com.au

Quantification of energy level alignments!

Switchable Ferroelectric Tunnel Junction for memory

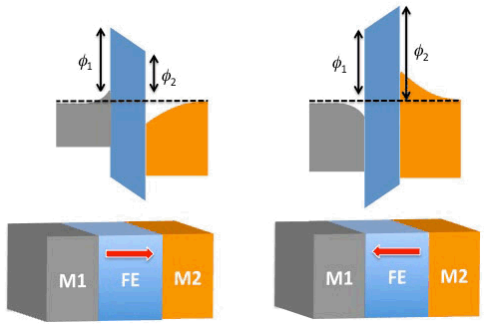
Ferroelectricity is an equilibrium phenomena of switchable polarization that can be used to prepare tunnel junctions.

A switchable, permanent polarization enables switchable, permanent resistances via tunneling.*

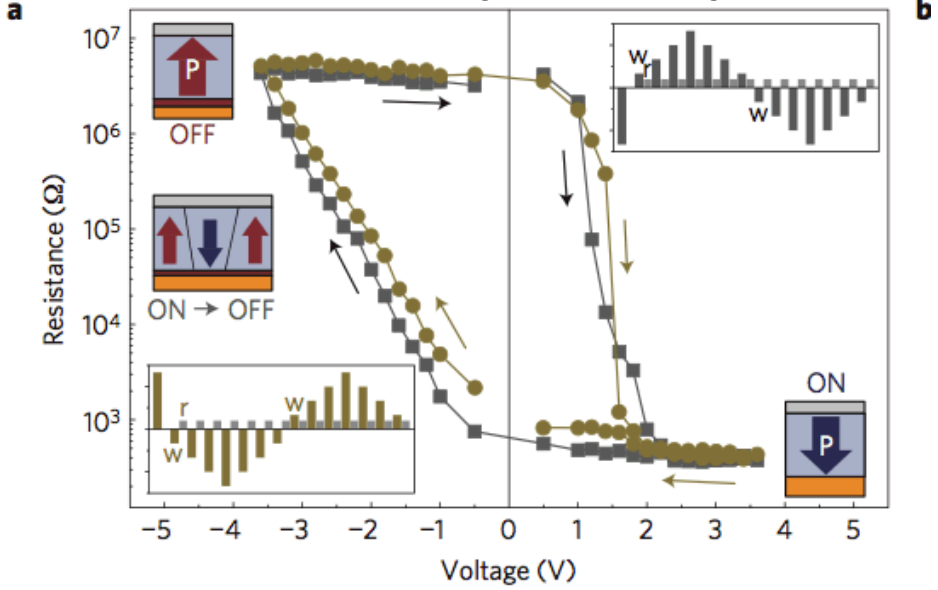
Must be thin enough for tunneling (<5nm)

Goals:
Alternative to memristor
Reliable and repeatable device operation
Uniform over large areas
Compatible with silicon fabrication processes

Tunnel barrier height dependence of ferroelectric polarization for a structure with dissimilar metal electrodes. Tunneling current is exponentially proportional to the square root of the barrier height.



$Pt/BaTiO_3/Nb:SrTiO_3$



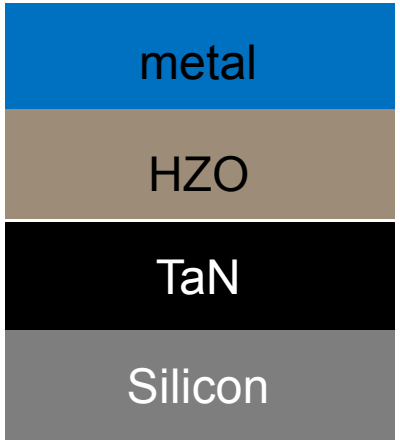
Wen *et al.*, Nat. Mater. 12, 617 (2013)

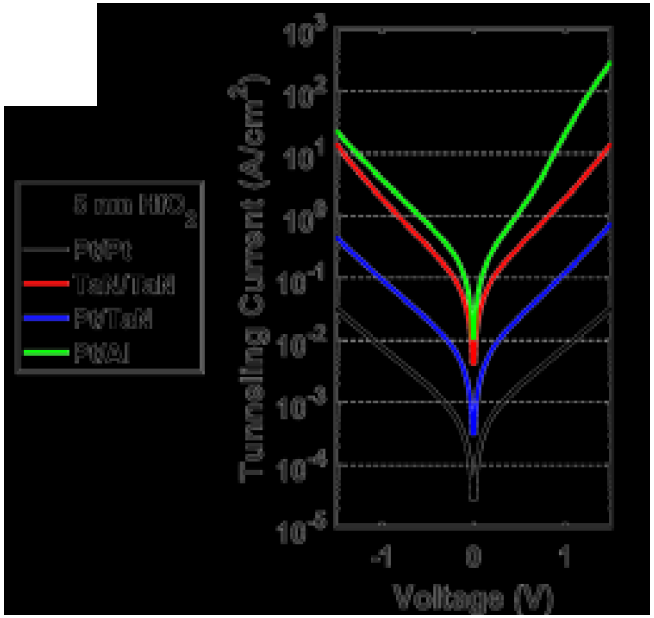
*Kohlstedt, et al. Phys. Rev. B **72**, 125341 (2005)

Application to Ferroelectrics

hafnium zirconium oxide ($Hf_xZr_{1-x}O_2$)

The recent demonstration of ferroelectric behavior in HfO_2 based thin films provides a silicon compatible ferroelectric process for such devices. Changing the polarization state of a thin ferroelectric layer will change the resistance between two metal electrodes.

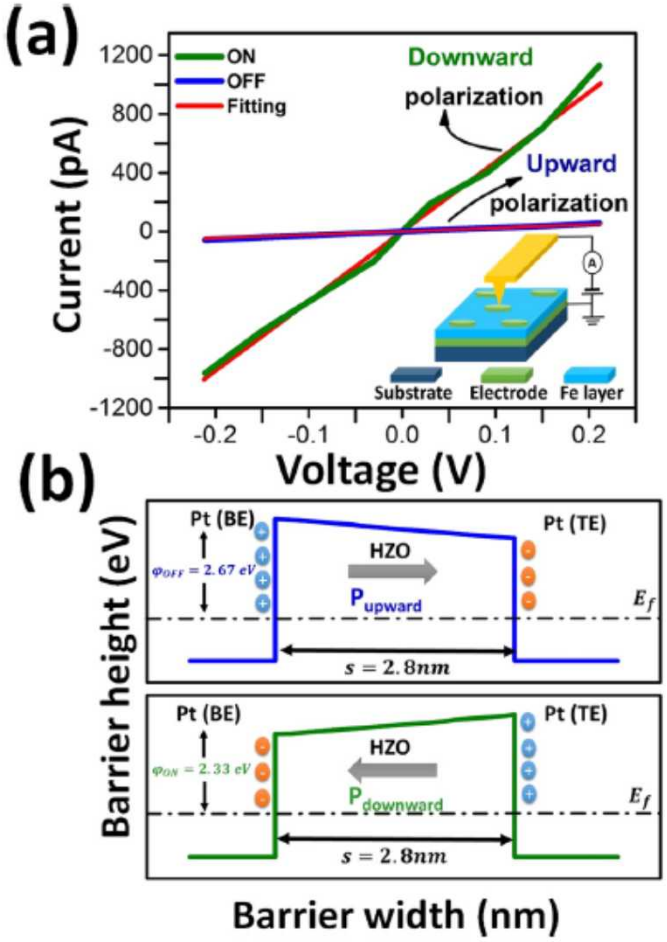


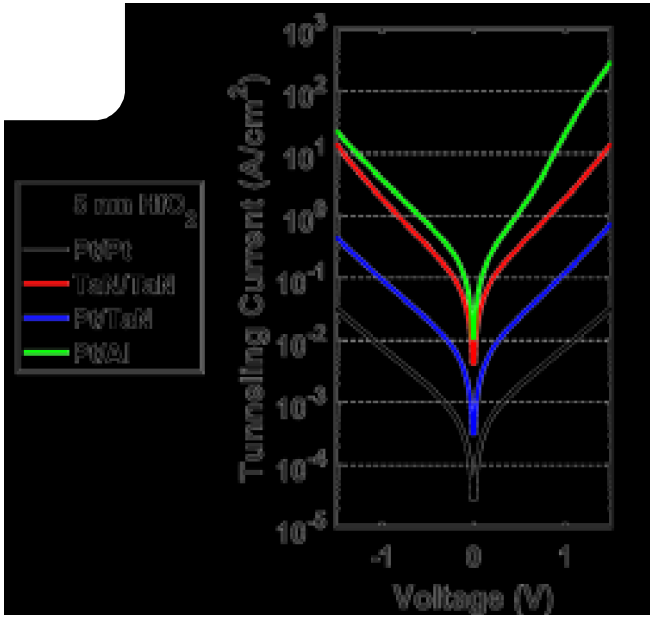


modeled tunneling currents, based off of band offset measurements for 5 nm of $(Hf,Zr)O_2$

Boscke, Muller, Brauhaus, Schroder, Bottger, "Ferroelectricity in hafnium oxide thin films," *Appl. Phys. Lett.*, **99** [10] 102903 (2011).

Application to Ferroelectrics





modeled tunneling currents, based off of band offset measurements for 5 nm of $(Hf,Zr)O_2$

APPLIED PHYSICS LETTERS **110**, 093106 (2017)

Tunneling electroresistance effect in a $Pt/Hf_{0.5}Zr_{0.5}O_2/Pt$ structure

F. Ambriz-Vargas,[1,a)] G. Kolhatkar,[1] R. Thomas,[1] R. Nouar,[2] A. Sarkissian,[2] C. Gomez-Yáñez,[3] M. A. Gauthier,[1] and A. Ruediger[1,a)]
[1]*Centre Énergie, Matériaux et Télécommunications, INRS, Varennes, Québec J3X1S2, Canada*
[2]*Plasmionique Inc., 9092 Rimouski, Brossard, Québec J4X 2S3, Canada*
[3]*Departamento de Ingeniería en Metalurgia y Materiales-Instituto Politécnico Nacional, Zacatenco 07738, Mexico*

(Received 6 September 2016; accepted 7 February 2017; published online 1 March 2017)

How to quantify VBO from XPS

of citations:
APS = 734
Web of Science = 625
Google Scholar = 735

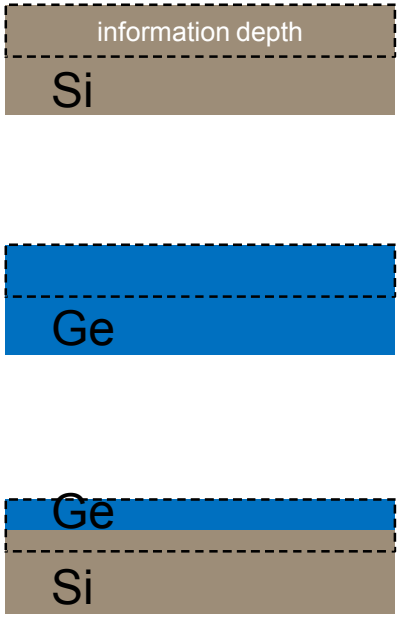
VOLUME 44, NUMBER 24 PHYSICAL REVIEW LETTERS 16 JUNE 1980

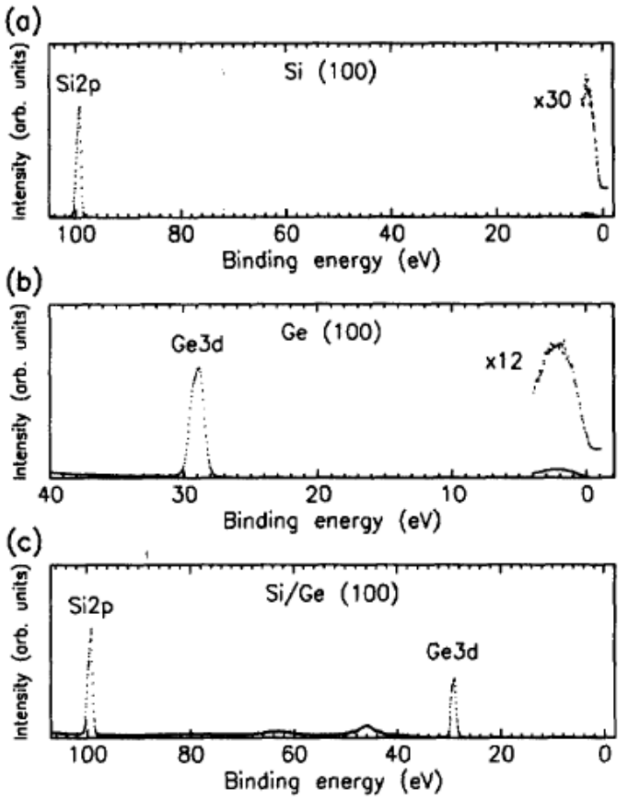
Precise Determination of the Valence-Band Edge in X-Ray Photoemission Spectra: Application to Measurement of Semiconductor Interface Potentials

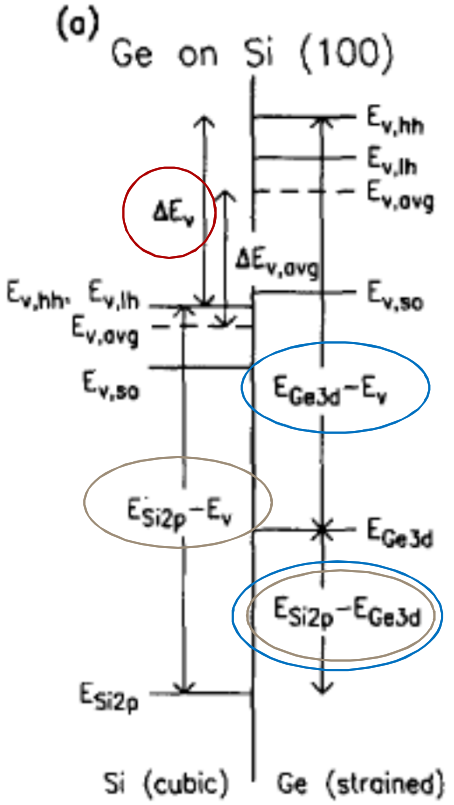
E. A. Kraut, R. W. Grant, J. R. Waldrop, and S. P. Kowalczyk
Rockwell International Electronics Research Center, Thousand Oaks, California 91360

(Received 26 December 1979)

$$\Delta E_v = (E^{Ge}_{Ge\,3d} - E^{Ge}_{v}) + (E^{Si}_{Si\,2p} - E^{Ge}_{Ge\,3d}) - (E^{Si}_{Si\,2p} - E^{Si}_{v}).$$

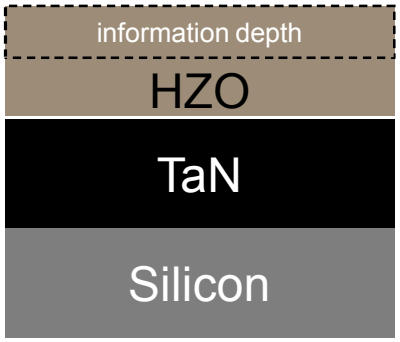




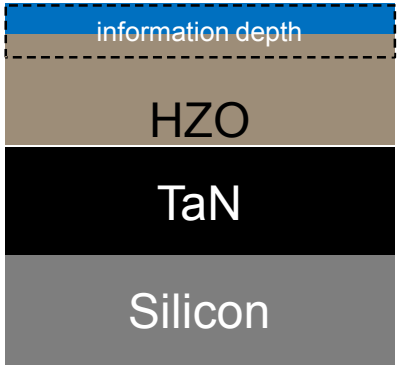


Advantages: (1) requires only three samples (2) reference to E_{vac} not necessary (3) ex situ samples

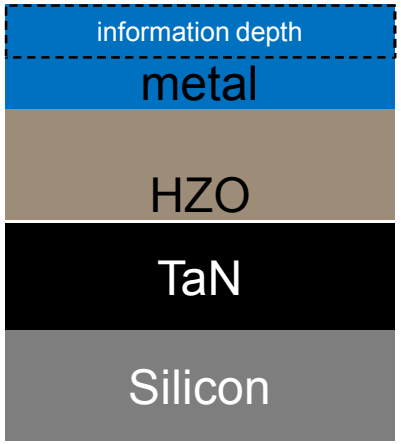
FTJ heterostructures for VBO determination



"HZO"
50/50 hafnium zirconium oxide
"substrate"



"intermediate"
"interlayer"
"interface"



"bulk"
"overlayer"

Ta
TaN
Pt
Au
Ni
Al

Calibration/Linearity of X-axis

Designation: E 2108 – 00

Standard Practice for
Calibration of the Electron Binding-Energy Scale of an X-Ray Photoelectron Spectrometer[1]

This standard is issued under the fixed designation E 2108; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

TABLE 3 Reference Binding Energies, $E_{ref\ n}$ for the Peaks Used in the Calibration Procedure for the Indicated X-Ray Sources (1,2)

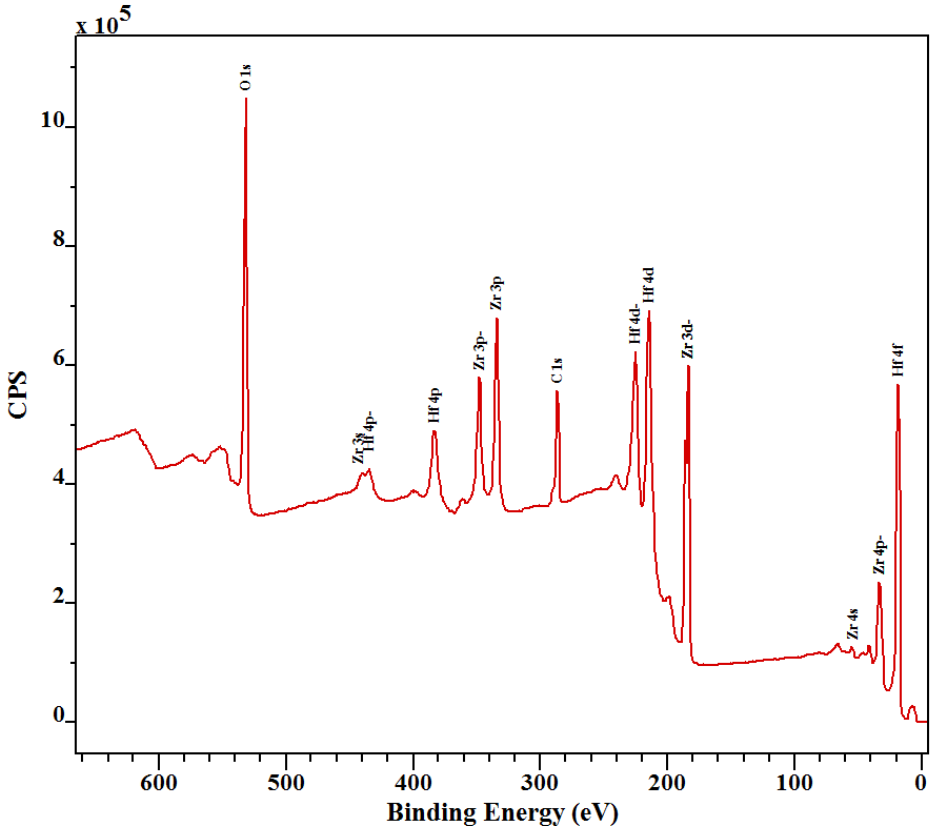
NOTE 1—The Ag data included in parentheses are not used normally in the calibration.

Peak Number, *n*	Assignment	$E_{ref\ n}$(eV) Al Kα	Mg Kα	Monochro-matic Al Kα
1	Au $4f_{7/2}$	83.95	83.95	83.96
2	Ag $3d_{5/2}$	(368.22)	(368.22)	368.21
3	Cu L_3VV	567.93	334.90	-
4	Cu $2p_{3/2}$	932.63	932.62	932.62

	Pass Energy	Position	ASTM	Difference
gold	40	84.03	83.96	0.07
	20	**83.95**	**83.96**	**-0.01**
	10	83.98	83.96	0.02
	5	83.97	83.96	0.01
silver	40	368.29	368.21	0.08
	20	**368.22**	**368.21**	**0.01**
	10	368.22	368.21	0.01
	5	368.24	368.21	0.03
copper	40	932.62	932.62	0.00
	20	**932.60**	**932.62**	**-0.02**
	10	932.58	932.62	-0.04
	5	932.60	932.62	-0.02

Minimize effects from non-linearity and/or charging

Use peaks with low binding energies.
(1) minimize effects from any non-linearity in X-axis
(2) peaks are more representative of valence structure

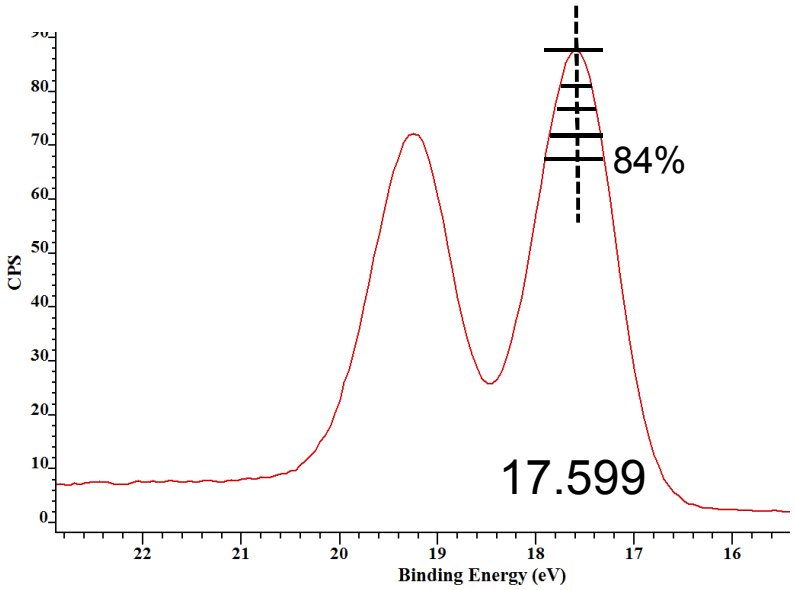


Determination of core level position

Sandia National Laboratories

Designation: E 2108 – 00

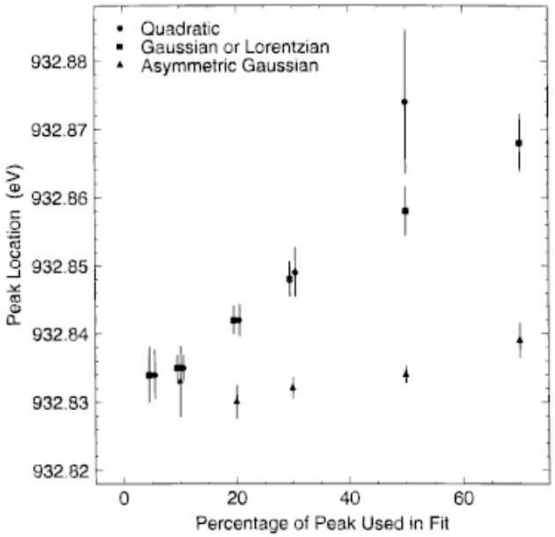
8.8.1.3 Draw chords horizontally across the peak at an intensity of 84 % of the maximum peak height (above zero counts) and at three or more further intensities approximately equally spaced in the range 84 to 100 % of the maximum peak height (above zero counts). Locate the midpoints of the chords. Draw a line through these midpoints; alternatively, a linear least-squares fit can be made to the positions of the chord midpoints. Obtain the energy for the peak maximum from the intersection of the line with a linear segment drawn to connect two data points in the vicinity of the peak maximum.

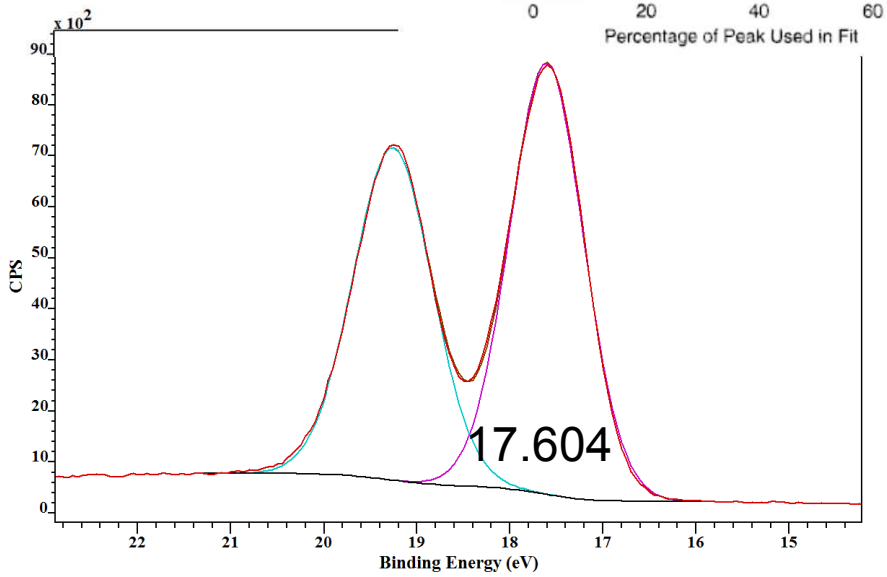


SURFACE AND INTERFACE ANALYSIS, VOL. 25, 777–787 (1997)

Energy Calibration of X-ray Photoelectron Spectrometers. II. Issues in Peak Location and Comparison of Methods

C. J. Powell*
Surface and Microanalysis Science Division, National Institute of





…or, take the derivative (17.600 eV)

Determination of Valence Band Edge

Band offsets in transition-metal oxide heterostructures

To cite this article: I Goldfarb *et al* 2013 *J. Phys. D: Appl. Phys.* **46** 295303

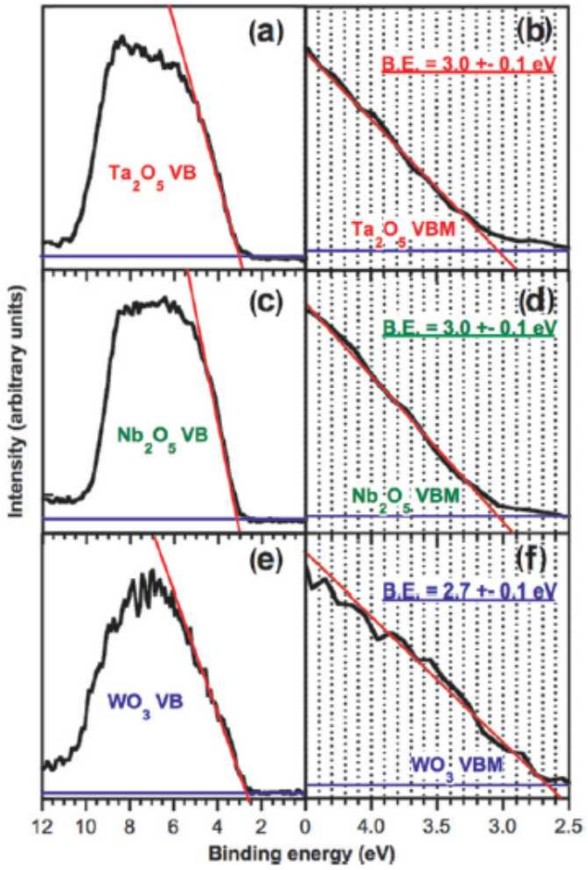
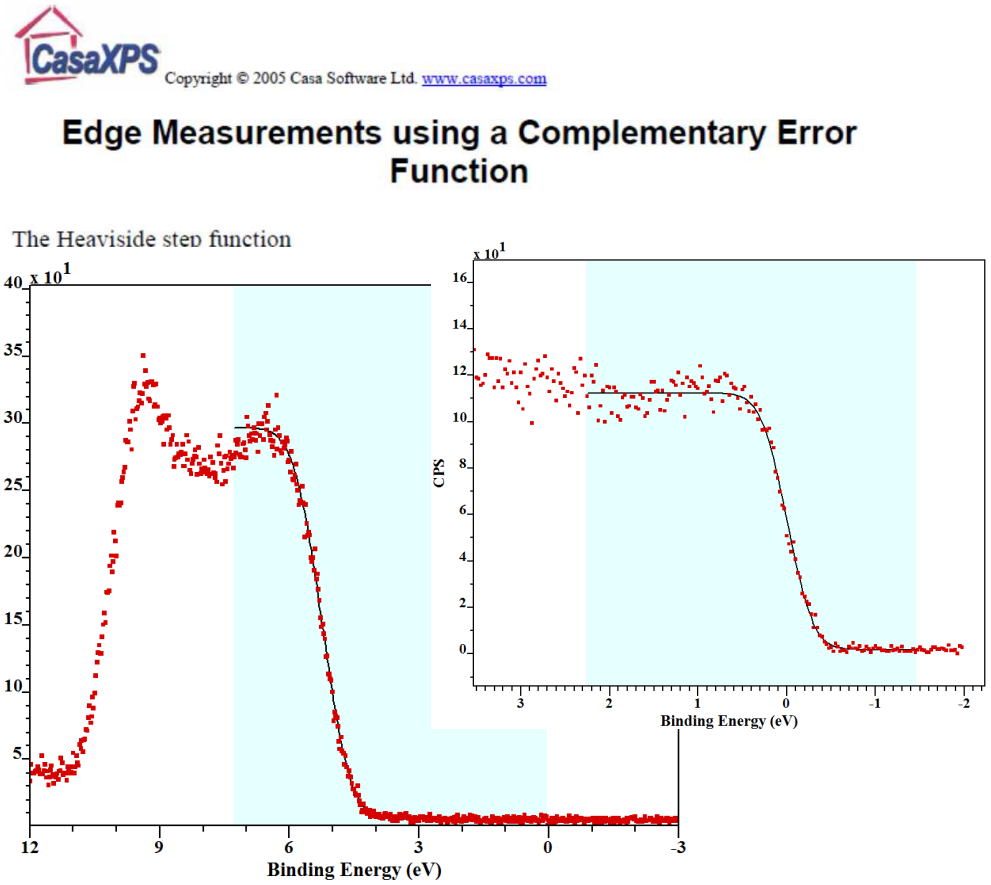


Figure 1. Precise determination of the valence band maxima (VBM) for the thick individual Ta_2O_5, Nb_2O_5 and WO_3 films.

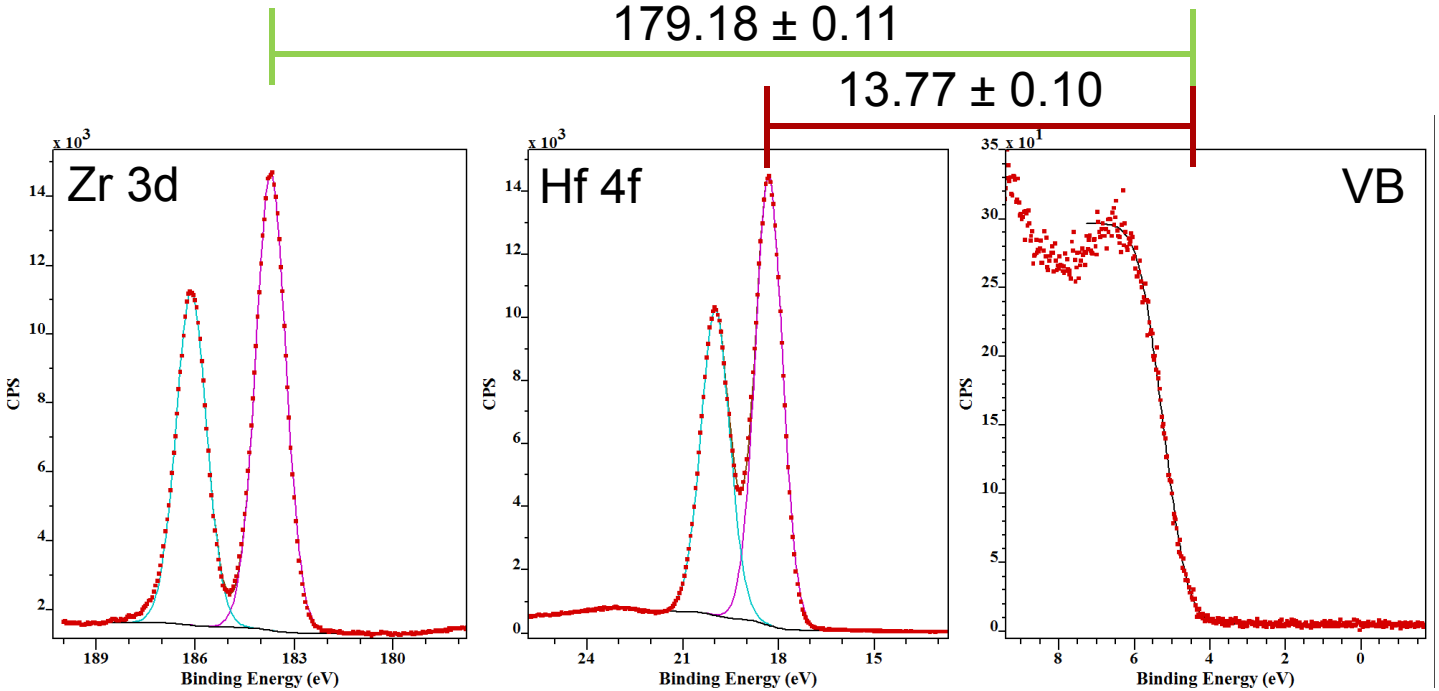
Extrapolation to linear regions of baseline and valence band cut-off.



Comparison to DOS from DFT

Effect of different core levels

For 7 different samples of HZO measured over the course of ~24 months…

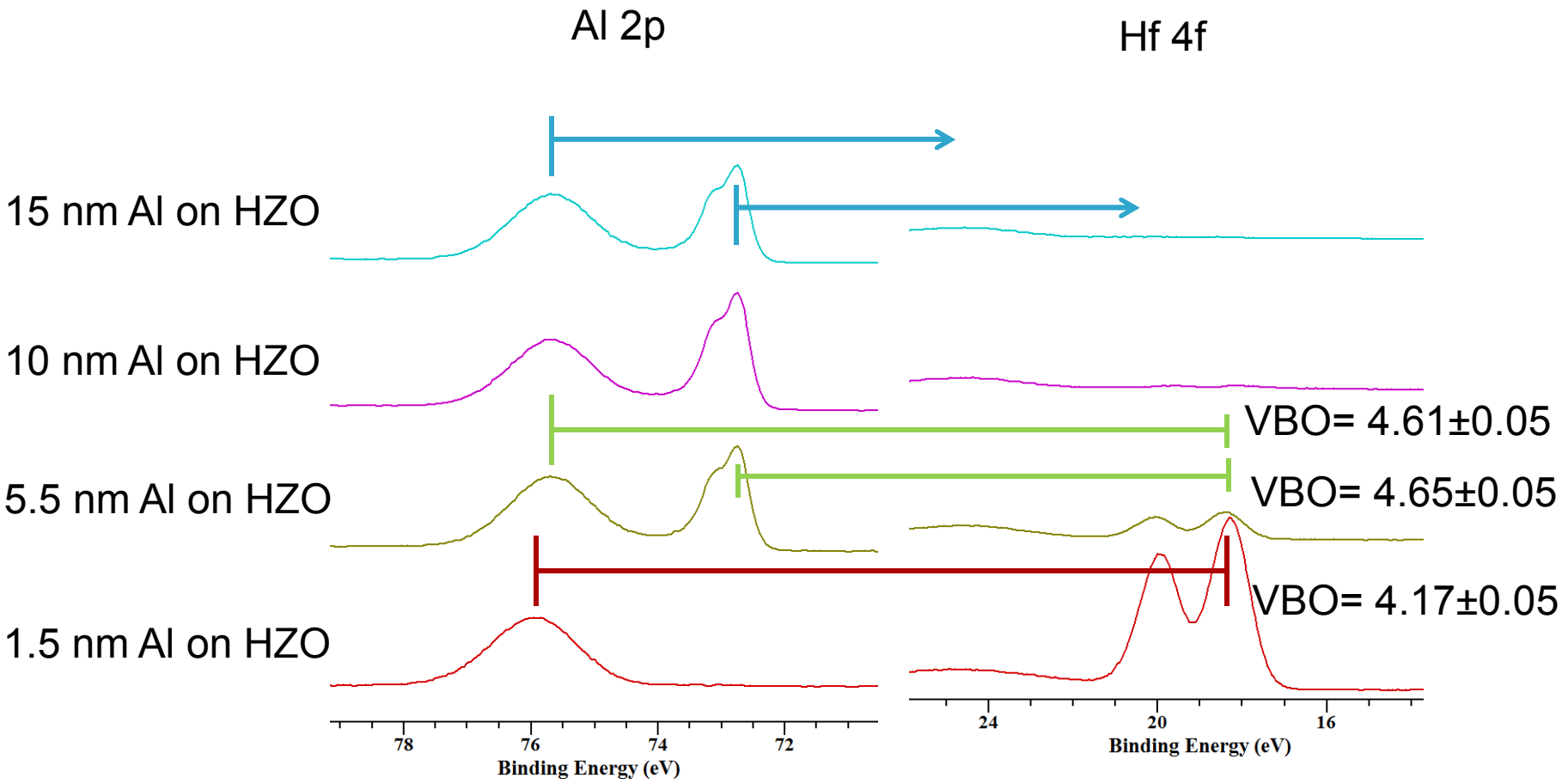


$$VBO = (E_{Ta\ 4f} - E_{VB})^{Ta} + (E_{Zr\ 3d} - E_{Ta\ 4f})^{HZO/Ta} - \mathbf{(E_{Zr\ 3d} - E_{VB})^{HZO}}$$

$$VBO = (E_{Ta\ 4f} - E_{VB})^{Ta} + (E_{Hf\ 4f} - E_{Ta\ 4f})^{HZO/Ta} - \mathbf{(E_{Hf\ 4f} - E_{VB})^{HZO}}$$

For HZO/Ta interface using:
Zr 3d → VBO= 3.24 ± 0.11
Hf 4f → VBO= 3.31 ± 0.10

Effect of oxide vs. metal components

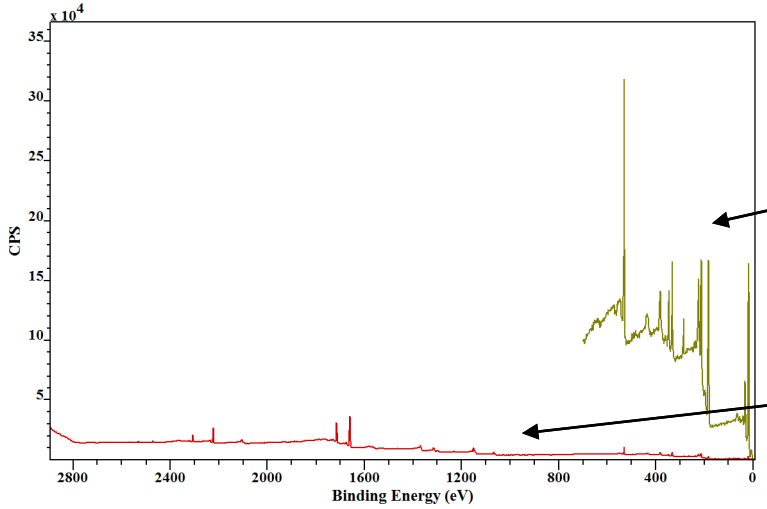


$$VBO = (\mathbf{E}_{\mathbf{Al\ 2p}} - E_{VB})^{Al} + (E_{Hf\ 4f} - \mathbf{E}_{\mathbf{Al\ 2p}})^{HZO/Al} - (E_{Hf\ 4f} - E_{VB})^{HZO}$$

Standard deviation from measurements at multiple locations.

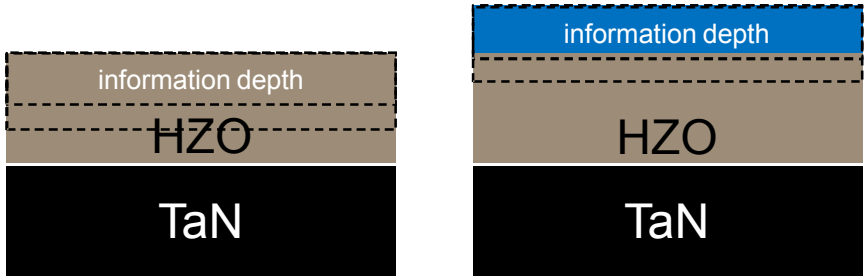
Ag vs. Al X-ray

hafnium zirconium oxide



hv = Al Kα @ 1486.7 eV

hv = Ag Lα @ 2984.2 eV

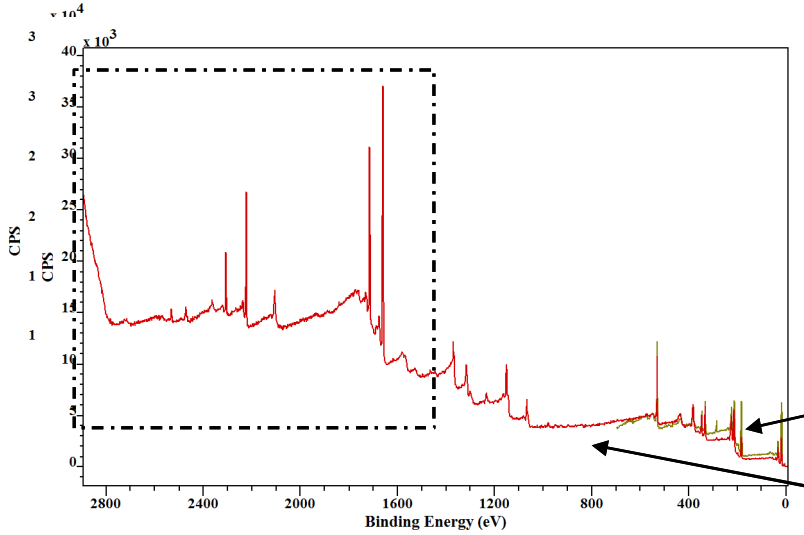


Universal curve for IMFP scales with $E^{0.78}$

Al → Ag doubles energy giving ~1.5x information depth

Ag vs. Al X-ray

hafnium zirconium oxide

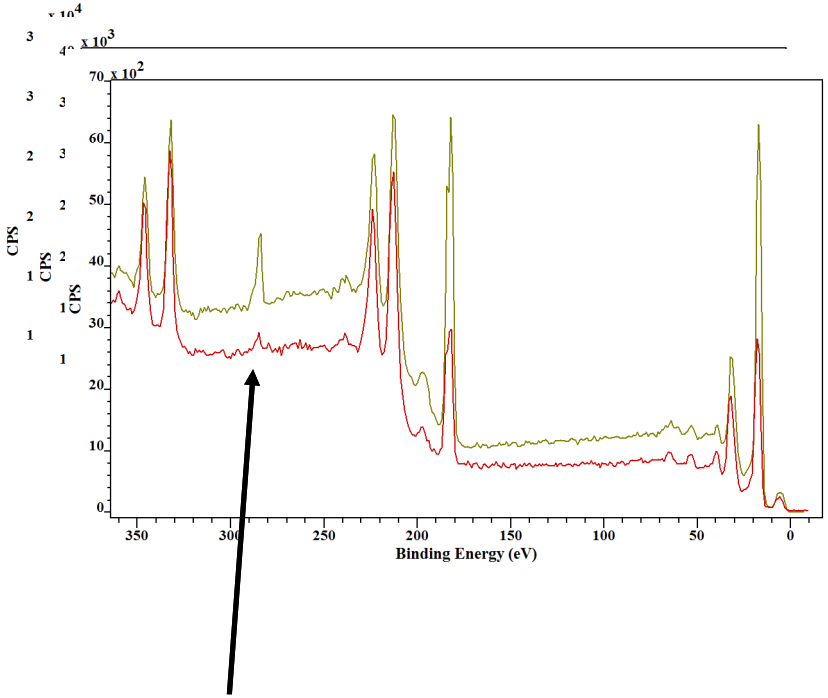


hv = Al Kα @ 1486.7 eV

hv = Ag Lα @ 2984.2 eV

Ag vs. Al X-ray

hafnium zirconium oxide

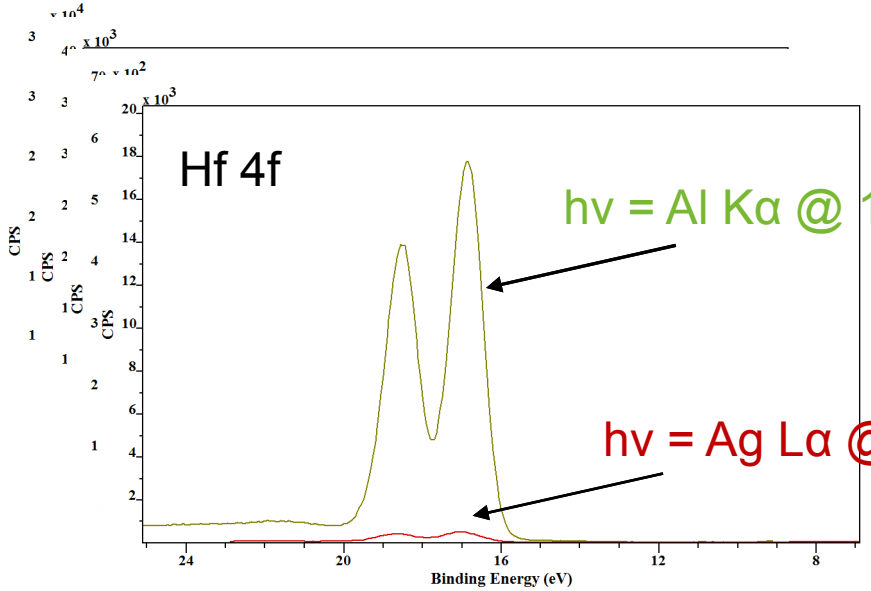


relative intensity of C 1s decreases
for higher energy X-ray excitation

normalized spectra show
comparable features

Ag vs. Al X-ray

hafnium zirconium oxide

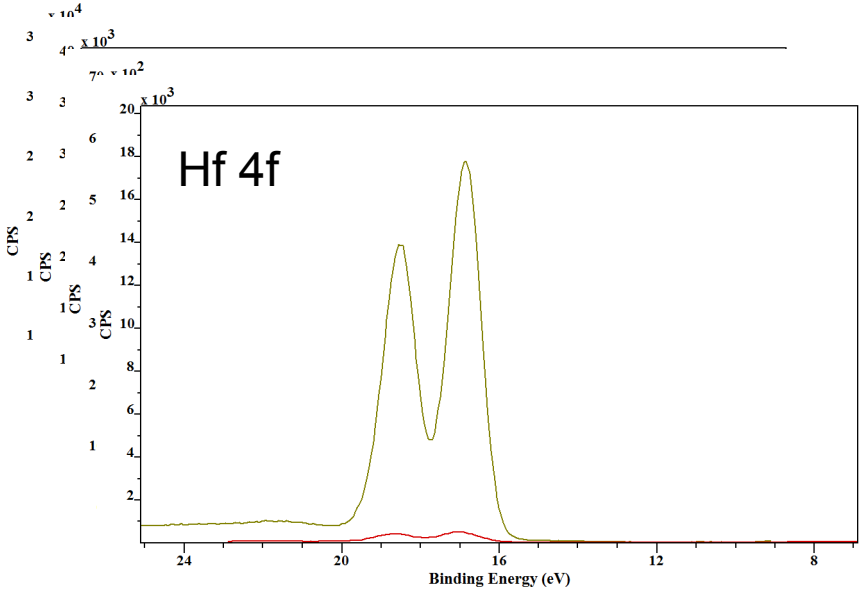


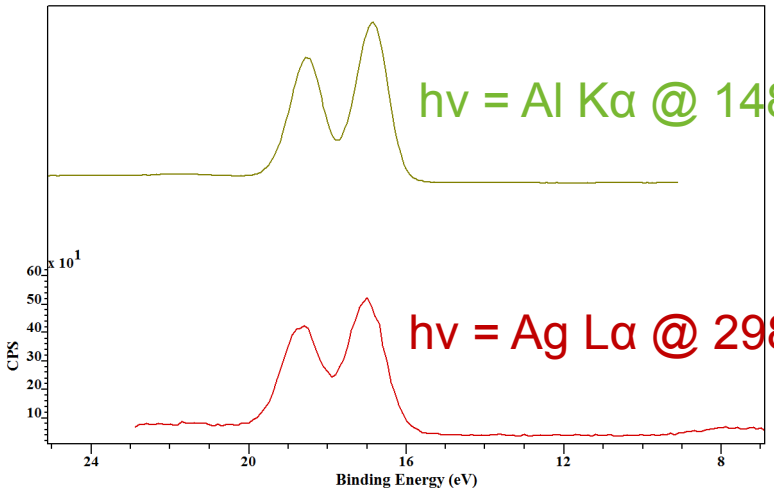
hv = Al Kα @ 1486.7 eV, PE 20

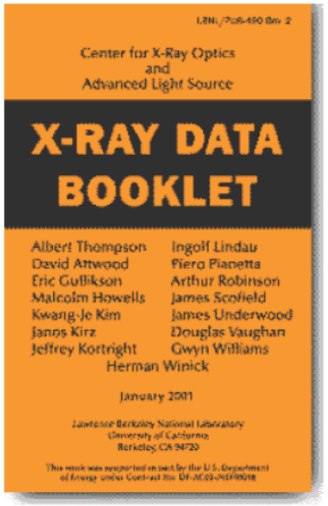
hv = Ag Lα @ 2984.2 eV, PE 40

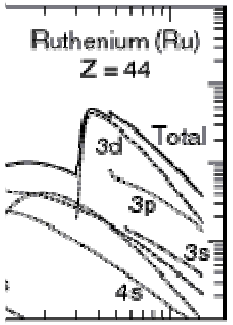
Ag vs. Al X-ray

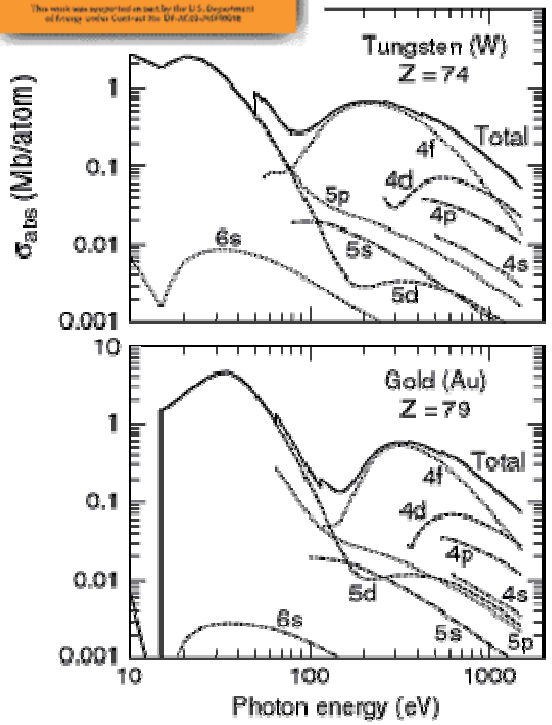
hafnium zirconium oxide





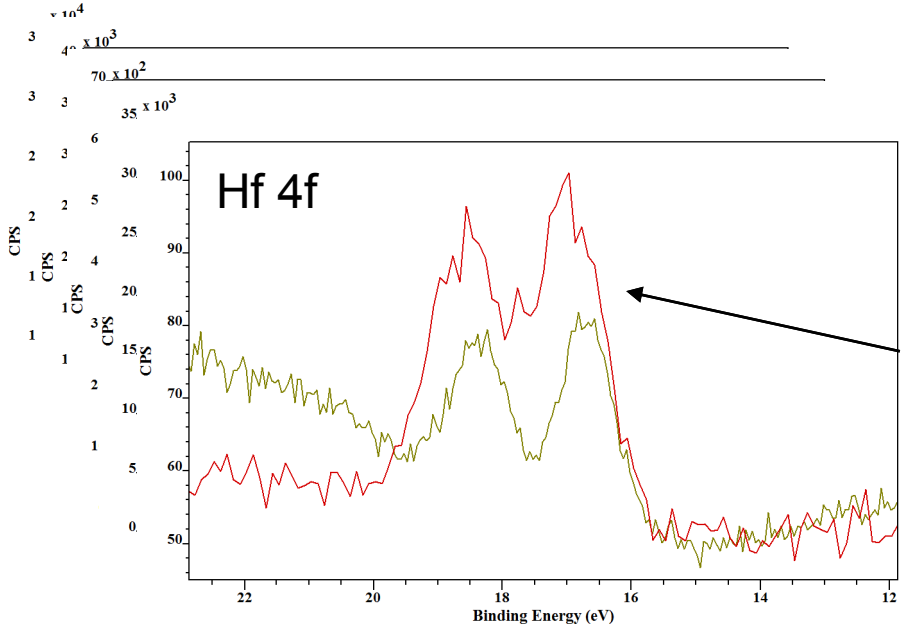






Ag vs. Al X-ray

Hf 4f from hafnium zirconium oxide through 5 nm Nickel



hv = Al Kα @ 1486.7 eV, PE 20

hv = Ag Lα @ 2984.2 eV, PE 40

…for HZO/Ni interface…

VBO = 3.31 on instrument 1

VBO = 3.29 on instrument 2, five months later

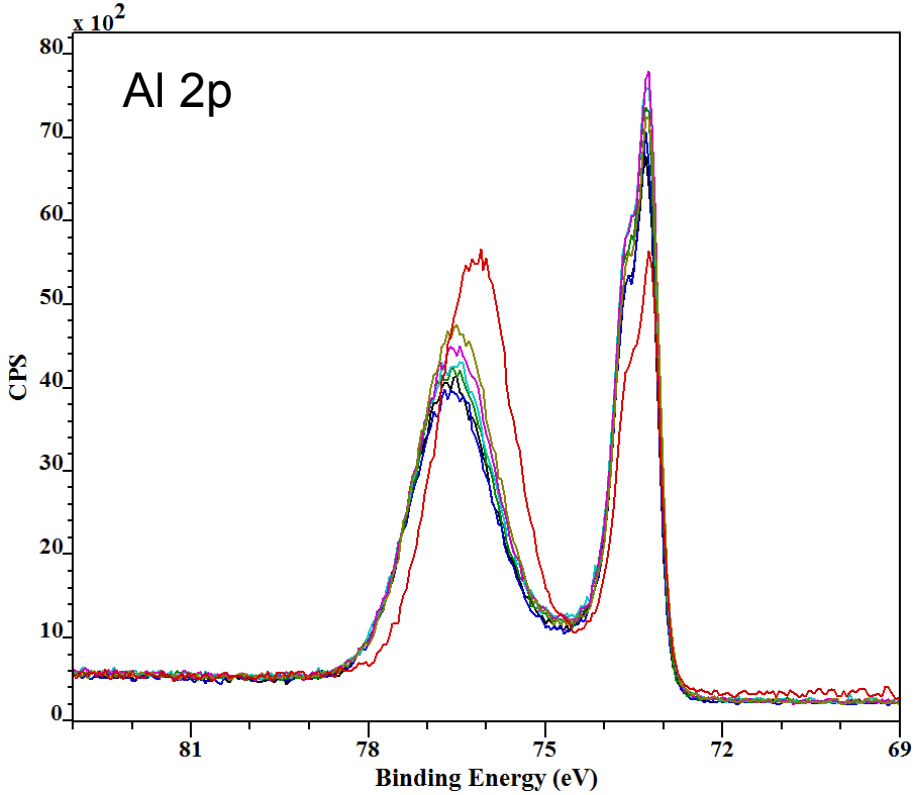
VBO = 3.44 on instrument 2 w/ Ag X-ray source

Ar^+ cluster sputtering – VBO from 1 sample?

Sandia National Laboratories

15 nm Al on HZO

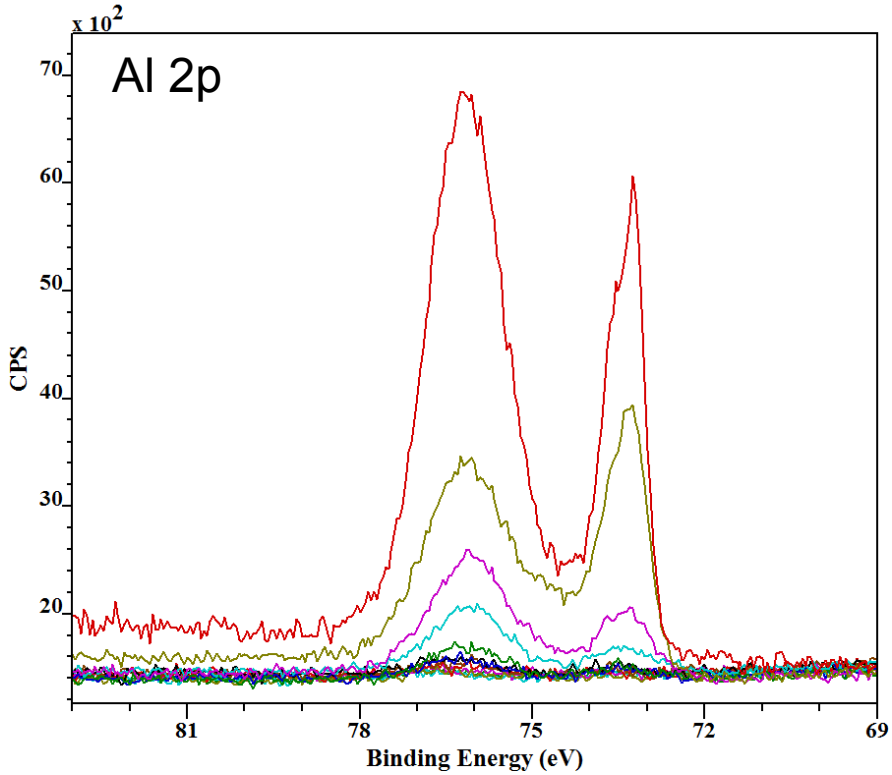
10 keV, 500⁺ Ar cluster – 60 sec. intervals



almost no sputtering of Aluminum

15 nm Al on HZO

15 keV, 500⁺ Ar cluster – 45 sec. intervals



sputter removal of Aluminum

Ar^+ cluster sputtering of Pt

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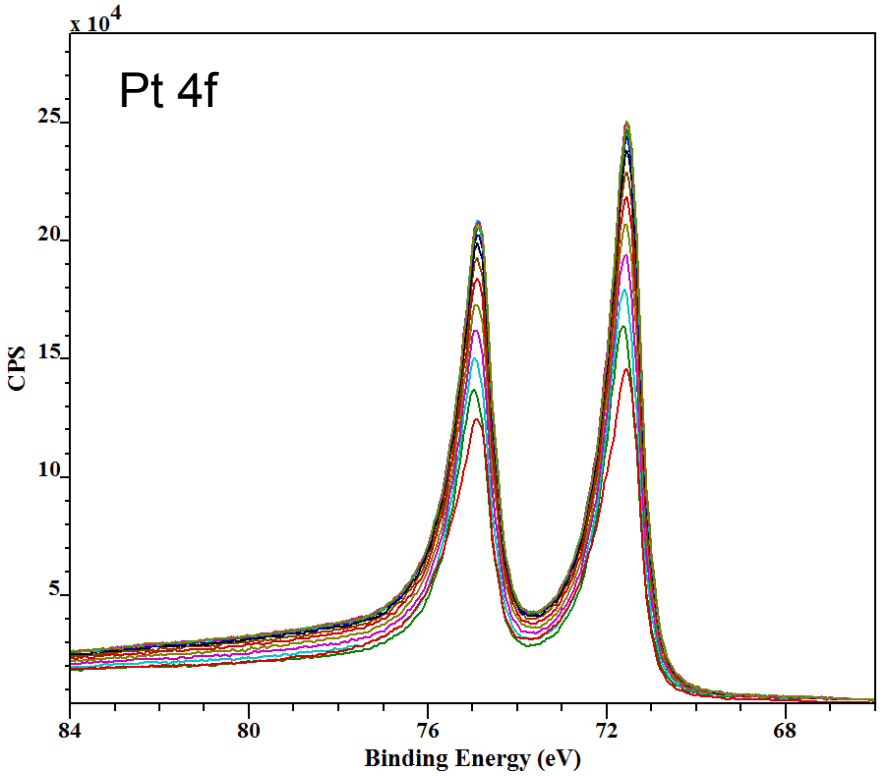
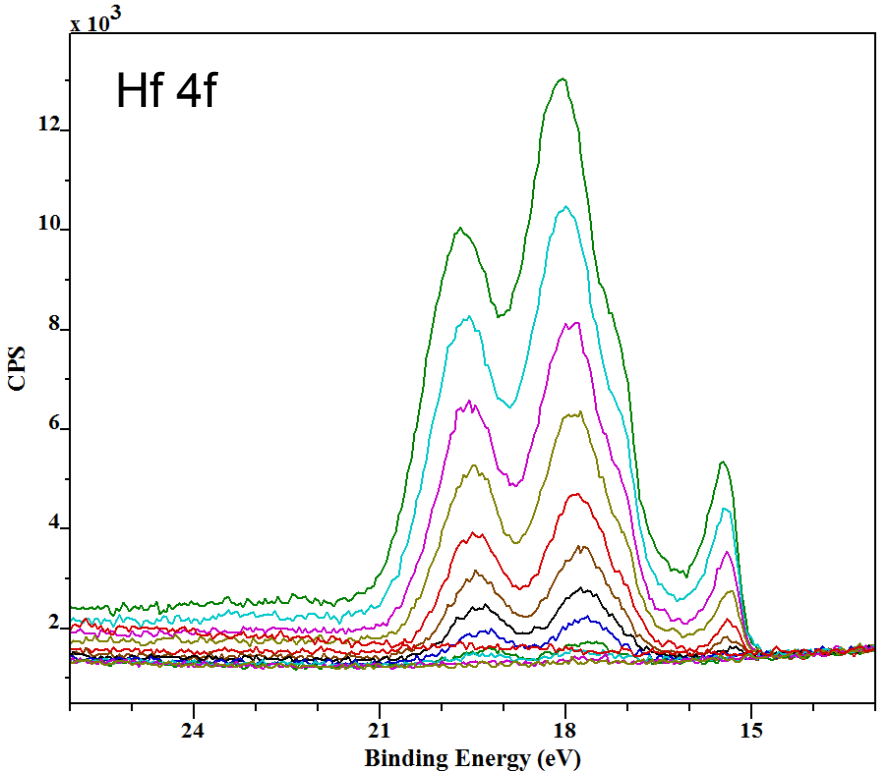
10 nm Pt on HZO

15 keV, 500⁺ Ar cluster – 45 sec. intervals



platinum slowly removed



metallic states of Hf observed

20 keV 250 Ar^+ cluster sputtering through Al/HZO/TaN layers

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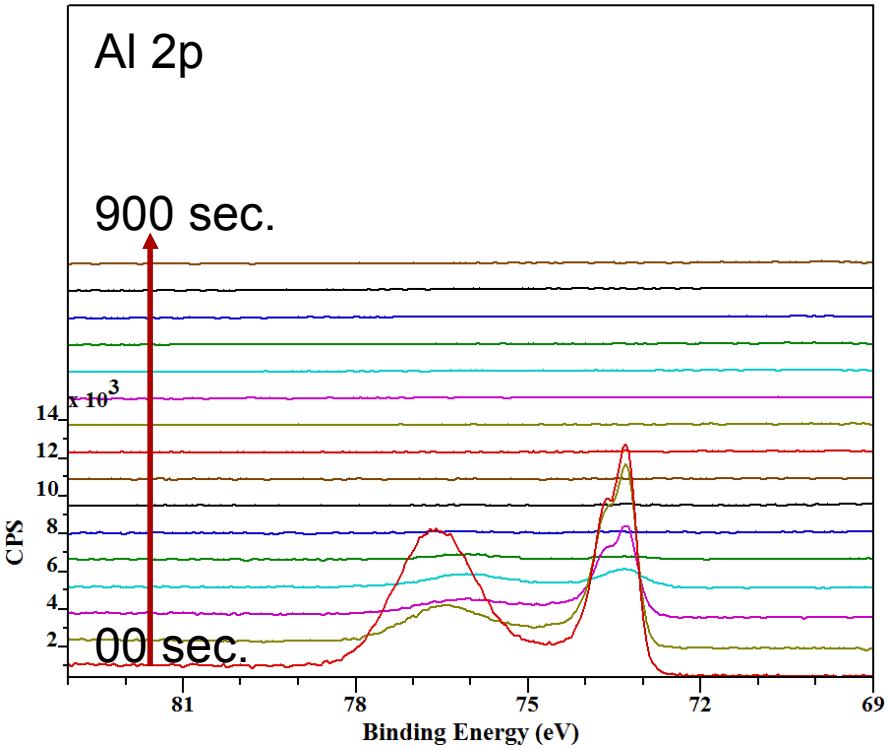
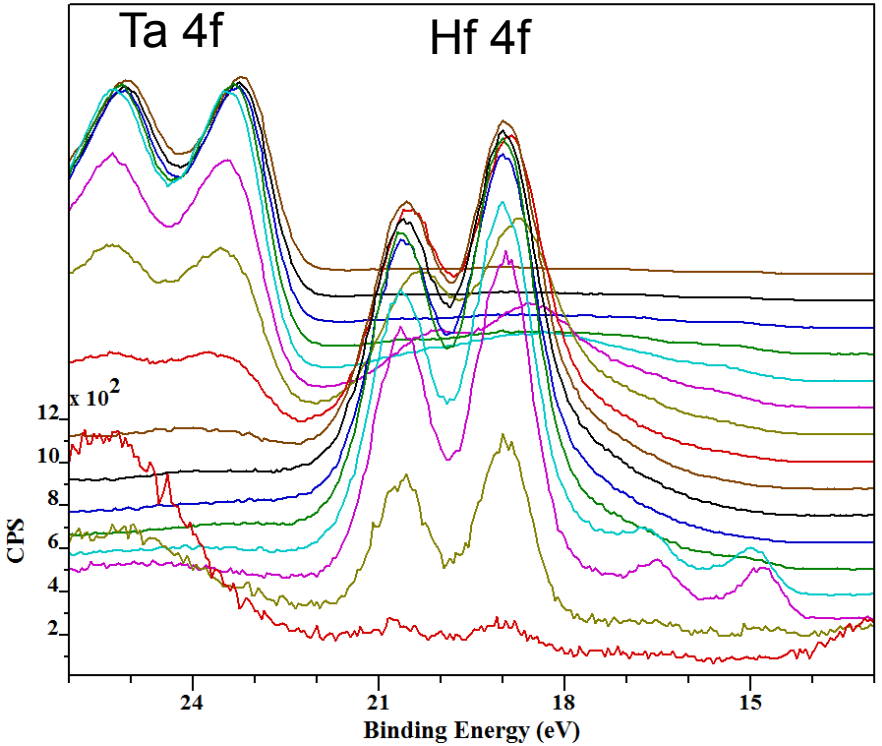
15 nm Al on HZO

20 keV, 250⁺ Ar cluster – 60 sec. intervals



aluminum rapidly removed



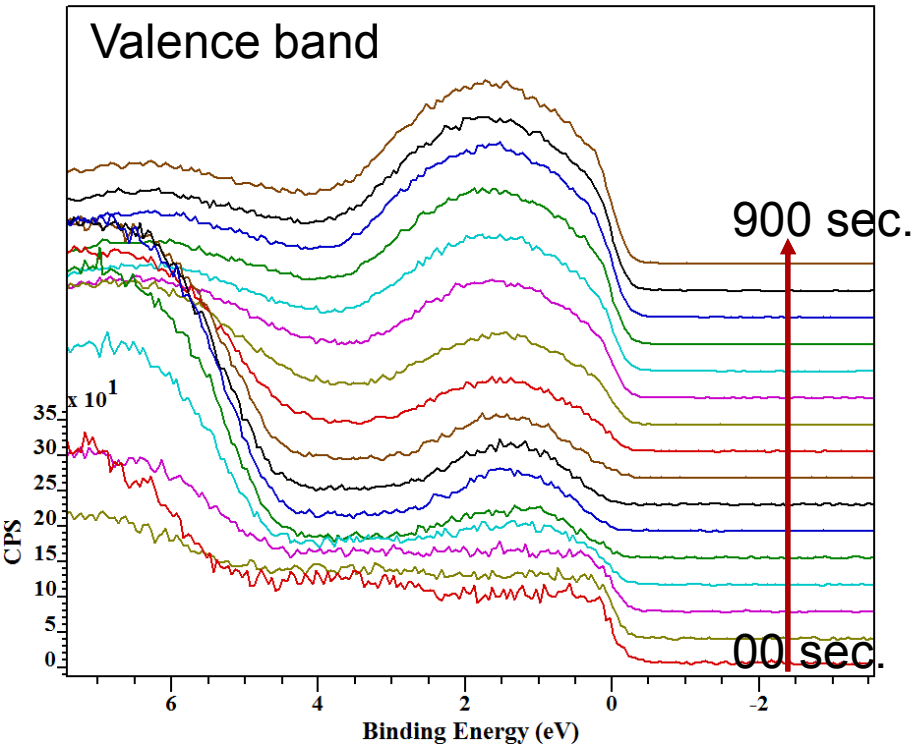
metallic states of Hf observed at early stages of sputtering

20 keV 250 Ar^+ cluster sputtering through Al/HZO/TaN layers

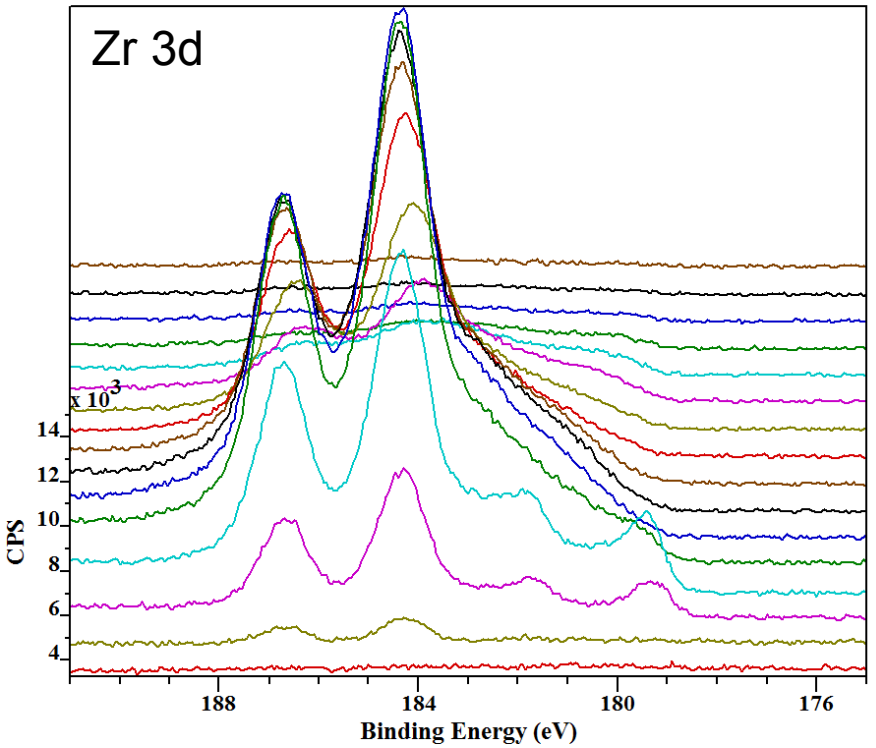
Sandia National Laboratories

15 nm Al on HZO

20 keV, 250⁺ Ar cluster – 60 sec. intervals

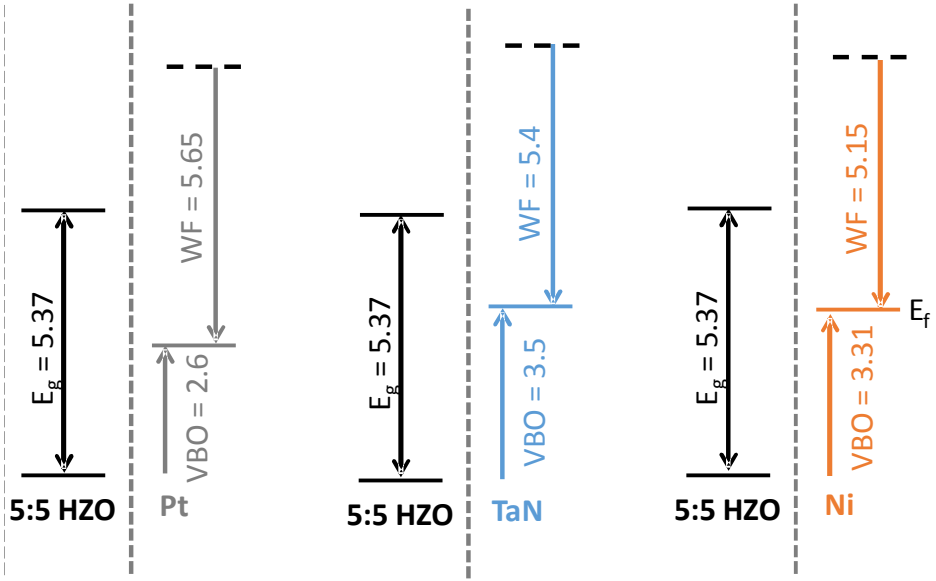


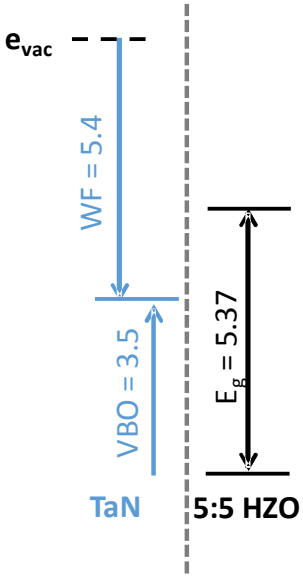
intensity observed in the valence band through entire depth profile

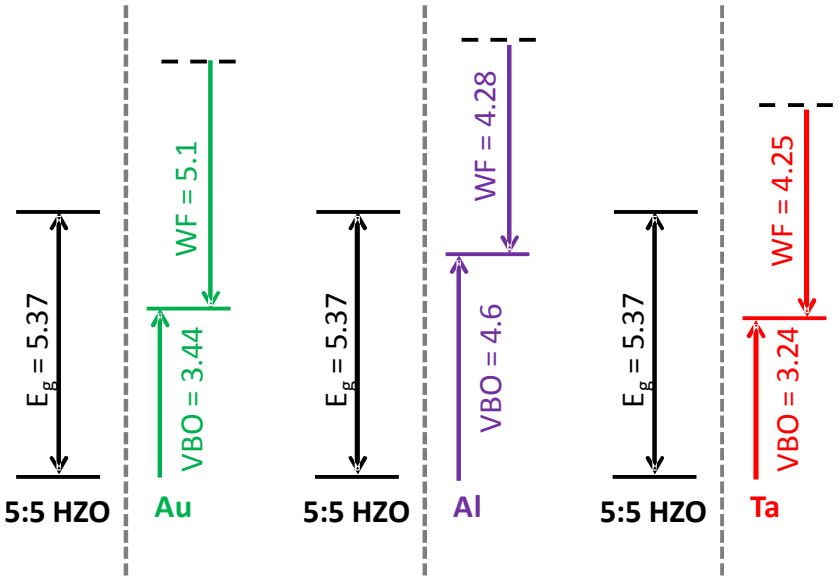


defects observed on Zr 3d peak through most of the HZO layer

Relevance to Ferroelectrics







E_g for HZO from Ambriz-Vargaz, et al. APL **110** 093106 (2017)

VBO for Pt/HZO = 2.7 eV

Chernikova, et al. ACS Appl. Mater. Interfaces 2016, 8, 7232-7237

Eg for HZO = 5.0 eV (REELS)

VBO for TiN/HZO = 3.3 eV

WF for TaN from kelvin probe

WF for metals from literature values (Michaelson, JAP **48** *11* (1977) 4729-4733.)

WF of HZO ~ 4.1 eV

Application to Ferroelectrics

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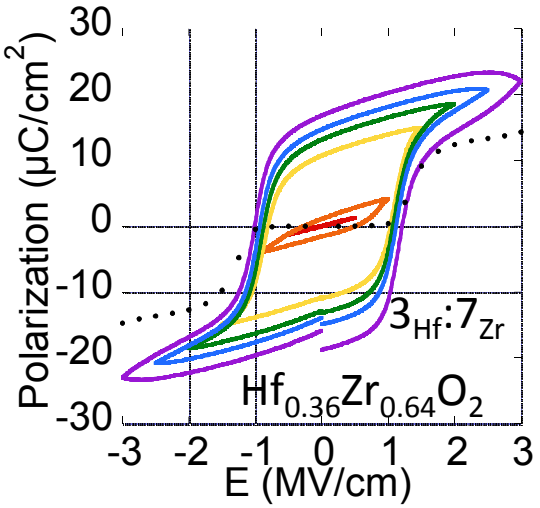
Dissimilar electrodes can enhance asymmetry of IV response.

$(Hf,Zr)O_2$ polarization very sensitive to electrode material

- Non TiN or TaN electrodes decrease polarization

20 nm $(Hf,Zr)O_2$ with TaN bottom and Pt top electrodes

- Slightly lower Polarization response



Example nested polarization loop (colored lines) and pulsed positive up negative down measured remanent polarization values (black dots) for 20 nm $(Hf,Zr)O_2$ deposited with a 3 HfO_2 to 7 ZrO_2 cycle ratio, TaN top and bottom electrodes and a 600 °C 30 s nitrogen gas anneal. The inset composition as measured by XPS.

Conclusions

- The method described by Kraut, Waldrop, Grant is a robust method for calculating valence band offsets for flat band diagrams.
- Calibration and linearity of the binding energy scale are important for accurate measurements.
- A consistent method for determining peak positions should be used. Peak fitting is sufficient for simple peak shapes.
- The use of hard X-rays to increase the information depth is a promising tool for VBO determinations when thick overlayers are present.
- Sputter depth profiling leads to defects in the films and is not recommended for VBO determination.
- Aluminum was found to have the largest VBO, smallest barrier, with HZO. However, device integration with aluminum is too complicated to be a viable strategy.

special thanks to…

Rebecca Chow, Dennis Robinson Brown, Ana Baca

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