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C. Zborowski; A. Vanleenhove; I. Hoflijk; ... et. al

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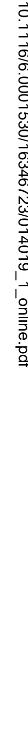
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High-energy x-ray photoelectron spectroscopy spectra of HfO_2 measured by Cr Kα

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Note: This paper is part of the 2022 Special Topic Collection on Higher Energy X-ray Photoelectron Spectroscopy.

ABSTRACT

Hafnium oxide (HfO_2) grown by atomic layer deposition on Si was analyzed using high-resolution high-energy x-ray photoelectron spectroscopy (HAXPES). The HAXPES spectra of HfO_2 obtained using monochromatic Cr Kα radiation at 5414.8 eV include two survey scans (Al Kα and Cr Kα) and high-resolution spectra of Hf 3s, Hf $3p_{3/2}$, Hf $3d_{5/2}$, Hf $4p_{3/2,}$ Hf 4d, Hf 4f, Hf 4s, and O 1s.

Key words: HfO_2, HAXPES, Cr Kα

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Accession #:01739 and 01743
Technique: XPS
Host Material: HfO_2
Instrument: ULVAC-PHI Quantes
Major Elements in Spectra: Hf, O
Minor Elements in Spectra: None
Published Spectra: 10
Spectra in Electronic Record: 10
Spectral Category: Comparison

INTRODUCTION

While high-energy photoemission has been in use for decades, only very few reference spectra are available, even for common materials. The recent availability of performant lab-scale photoemission spectrometers (Refs. 1–3) requires reliable reference data.

In this work, we present reference spectra from hafnium oxide (HfO_2) grown by atomic layer deposition (ALD) on Si, which was analyzed using high-resolution high-energy x-ray photoelectron spectroscopy (HAXPES). The HAXPES spectra of HfO_2 obtained using monochromatic Cr Kα radiation at 5414.8 eV include two survey scans (Al Kα and Cr Kα) and high-resolution spectra of Hf 3s, Hf $3p_{3/2}$, Hf $3d_{5/2}$, Hf $4p_{3/2,}$ Hf 4d, Hf 4f, Hf 4s, and O 1s.

SPECIMEN DESCRIPTION (ACCESSION # 01739)

Host Material: HfO_2
CAS Registry #: 12055-23-1
Host Material Characteristics: Homogeneous; solid; amorphous; dielectric; inorganic compound; thin film
Chemical Name: Hafnium oxide
Source: ALD grown
Host Composition: Hf, O
Form: Thin Film
Structure: Amorphous
History and Significance: Air exposed ALD HfO_2. The growth was performed using $HfCl_4$ and H_2O as precursors at 300 °C
As Received Condition: Piece of a 200 mm Si wafer
Analyzed Region: Same as host materials
***Ex Situ* Preparation/Mounting:** Sample was taped on the sample holder using insulating removable 3M double sided tape.
***In Situ* Preparation:** Before HAXPES measurement, the samples were cleaned with low energy Ar^+ ions (100 eV). The cleaning procedure was stopped when the carbon level was reduced to a negligible level using Al Kα radiation.
Charge Control: Low energy electrons (1 eV, filament 1.1 A) and low energy ions (10 eV, 5 mA emission)
Temp. During Analysis: 300 K
Pressure During Analysis: $<5 \times 10^{-7}$ Pa
Pre-analysis Beam Exposure: 0 s

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SPECIMEN DESCRIPTION (ACCESSION # 01743)

Host Material: Au
CAS Registry #: 7440-57-5
Host Material Characteristics: Homogeneous; solid; amorphous; conductor; metal; other
Chemical Name: Gold
Source: 0.250 mm thick foil from Goodfellow, AU000372/5
Host Composition: Au
Form: Bulk
Structure: Amorphous
History and Significance: In-vacuum sputtered
As Received Condition: Foil
Analyzed Region: Same as host materials
***Ex Situ* Preparation/Mounting:** The sample was taped on the sample holder using insulating removable 3M double sided tape.
***In Situ* Preparation:** Sample was sputtered using 1 keV Ar^+ ions until no C or O was observed.
Charge Control: Low energy electrons (1 eV, filament 1.1 A) and low energy ions (10 eV, 5 mA emission)
Temp. During Analysis: 300 K
Pressure During Analysis: $<5 \times 10^{-7}$ Pa
Pre-analysis Beam Exposure: 0 s

INSTRUMENT DESCRIPTION

Manufacturer and Model: ULVAC-PHI Quantes
Analyzer Type: Spherical sector
Detector: Multichannel resistive plate
Number of Detector Elements: 32

INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA

Spectrometer

Analyzer Mode: Constant pass energy
Throughput ($T = E^N$): The energy dependence can be modeled using the following equation: $A/E_p = (a^2/(a^2 + R^2))^b$, where a and b are constants, E_p is the pass energy, A is the peak area, and R is the retard ratio equal to E/E_p, where E is the kinetic energy. Three spectral regions [Ag 2s (3790–3830 eV), Ag 3s (700–740 eV), and Ag 3d (350–390 eV)] are recorded on a sputter-cleaned silver sample at different pass energies. The values of a and b are then determined to be 576.9 and 6.3, respectively, by a linear least square fit of the data applying the equation described above.
Excitation Source Window: Al
Excitation Source: Cr K_α monochromatic
Source Energy: 5414.8 eV
Source Strength: 43 W
Source Beam Size: $100 \times 100\,\mu m^2$
Signal Mode: Multichannel direct

Geometry

Incident Angle: 22°
Source-to-Analyzer Angle: 46°
Emission Angle: 45°
Specimen Azimuthal Angle: 0°
Acceptance Angle from Analyzer Axis: 0°
Analyzer Angular Acceptance Width: 20° × 20°

Ion Gun

Manufacturer and Model: ULVAC-PHI Quantes
Energy: 10 and 100 eV
Current: 5 mA
Current Measurement Method: Biased stage
Sputtering Species: Ar
Spot Size (unrastered): 10 000 μm
Raster Size: N/A
Incident Angle: 45°
Polar Angle: 45°
Azimuthal Angle: 45°
Comment: Gun used for neutralization

DATA ANALYSIS METHOD

Energy Scale Correction: Due to the too low intensity of the C 1s peak with Cr Kα, and the presputtering of the sample, the binding energy was referenced by determining the binding energy position of the Hf $4d_{5/2}$ peak recorded by Al Kα XPS measurement and subsequent correction shift of the C 1s peak to 284.8 eV. The determined binding energy position of Hf $4d_{5/2}$ is 213.14 eV. The binding energy shift of the Cr Kα data was then performed by shifting the Hf $4d_{5/2}$ peak to 213.14 eV.
Recommended Energy Scale Shift: 0.86 eV for binding energy
Peak Shape and Background Method: Data treatment was performed using Shirley background and Gaussian–Lorentzian peak shapes.
Quantitation Method: Quantification was done using PHI MULTIPAK Software Version 9.9.0.8. The elemental relative sensitivity factors were derived according to ISO 18118 Equation (A.7): "The pure-element relative sensitivity factor (PERSF), Si(Ep), can be obtained from measurements of Si(ref) for the selected element and a measurement of the peak intensity for the selected key material, I (key), as given in Formula (A.7): Si(Ep) = (Ii(ref)/(I(key))."

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material (Ref. 4).

REFERENCES

[1]See: https://www.ulvac-phi.com/en/products/xps/quantes/.
[2]See: https://www.kratos.com/products/axis-supra-xps-surface-analysis-instrument.
[3]See: https://scientaomicron.com/en/system-solutions/electron-spectroscopy/HAXPES-Lab.
[4]See supplementary material at https://doi.org/10.1116/6.0001530 for ASCII data of all shown spectra.

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SPECTRAL FEATURES TABLE

Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV × counts/s)	Sensitivity Factor	Concentration (at. %)[a]	Peak Assignment
01739-03	Hf 3s	2598.85	11.65	8180	1.552	42.6	HfO_2
01739-03[b]	Hf 3s satellite	2614.69	21.17	2852	…	…	HfO_2
01739-04	Hf $3p_{3/2}$	2107.41	6.37	24 315	4.794	42.5	HfO_2
01739-05	Hf $3d_{5/2}$	1661.91	2.29	35 593	8.342	42.8	HfO_2
01739-06	Hf $4p_{3/2}$	381.70	5.21	8389	1.783	43.7	HfO_2
01739-07	Hf $4d_{5/2}$	213.14	4.20	8812	1.695	50.5	HfO_2
01739-07	Hf $4d_{3/2}$	223.88	4.50	5906	1.119	50.5	HfO_2
01739-08	Hf $4f_{7/2}$	16.77	1.46	956	0.283	55.7	HfO_2
01739-08	Hf $4f_{5/2}$	18.42	1.46	713	0.212	55.7	HfO_2
01739-08[b]	O 2s	20.67	4.33	159	…	…	HfO_2
01739-09	O1s	530.27	1.72	2408	0.589	…	HfO_2
01739-09	O1s	531.79	1.72	285	0.589	…	Possible –OH
01739-09[b]	Hf 4s	536.44	6.06	2048	…	…	HfO_2

[a]The concentration is calculated by taking into account only the O 1s peak from HfO_2 and the Hf peak from the given transition.
[b]No experimental sensitivity factor available.

ANALYZER CALIBRATION TABLE[a]

Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV × counts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
01743-01	Au $3d_{5/2}$	2206.8	2.59	47 379	…	…	…
01743-01	Au $4f_{7/2}$	84.2	1.24	2 115	…	…	…
…	Cu $2p_{3/2}$	932.9	1.34	7 090	…	…	…
…	Ag $2p_{3/2}$	3352.7	2.61	30 352	…	…	…
…	Ag $3d_{5/2}$	368.4	1.15	2978	…	…	…

[a]The calibration table is established using the Cr Kα photons and a pass energy of 112 eV corresponding to the presented high-resolution spectra.

GUIDE TO FIGURES

Spectrum (Accession) #	Spectral Region	Voltage Shift[a] (eV)	Multiplier	Baseline	Comment #
01743-01	Survey	0	1	0	Au spectrum with x-ray source Cr Kα[b]
01739-01	Survey	0	1	0	X-ray source Al Kα
01739-02	Survey	0	1	0	X-ray source Cr Kα
01739-03	Hf 3s	–0.86	1	0	…
01739-04	Hf $3p_{3/2}$	–0.86	1	0	…
01739-05	Hf $3d_{5/2}$	–0.86	1	0	…
01739-06	Hf $4p_{3/2}$	–0.86	1	0	…
01739-07	Hf 4d	–0.86	1	0	…
01739-08	Hf 4f	–0.86	1	0	…
01739-09	O 1s	–0.86	1	0	…

[a]Voltage shift of the archived (as-measured) spectrum relative to the printed figure. The figure reflects the recommended energy scale correction due to a calibration correction, sample charging, flood gun, or other phenomenon.
[b]The reference spectrum included in this paper is the same as those included with other papers in this collection that use this x-ray source. This was intentional and not an error as submissions were requested to be accompanied by a wide-scan spectrum of sputter-cleaned gold taken on the same instrument and using the same settings as the wide-scan spectrum of the material or materials in the submission.

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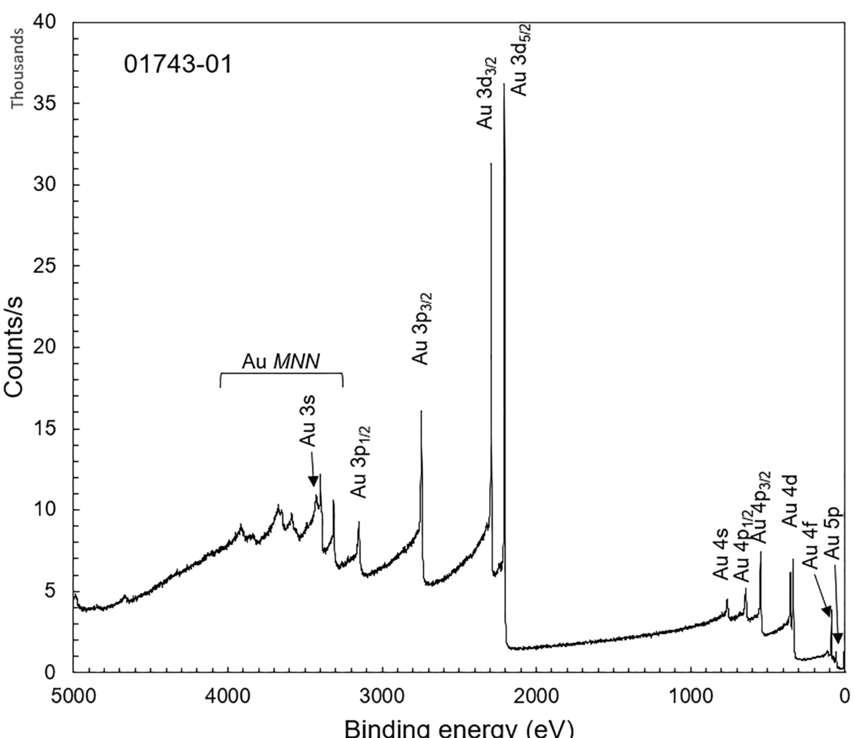

Accession #	01743-01
Host Material:	Au
Technique:	XPS
Spectral Region:	Survey
Instrument:	ULVAC-PHI Quantes
Excitation Source:	Cr K_α monochromatic
Source Energy:	8 eV
Source Strength:	9 W
Source Size:	0.1 × 0.1 mm^2
Analyzer Type:	Spherical sector analyzer
Incident Angle:	22°
Emission Angle:	45°
Analyzer Pass Energy:	280 eV
Analyzer Resolution:	1.9 eV
Total Signal Accumulation Time:	5210 s
Total Elapsed Time:	5700 s
Number of Scans:	1
Effective Detector Width:	31 eV

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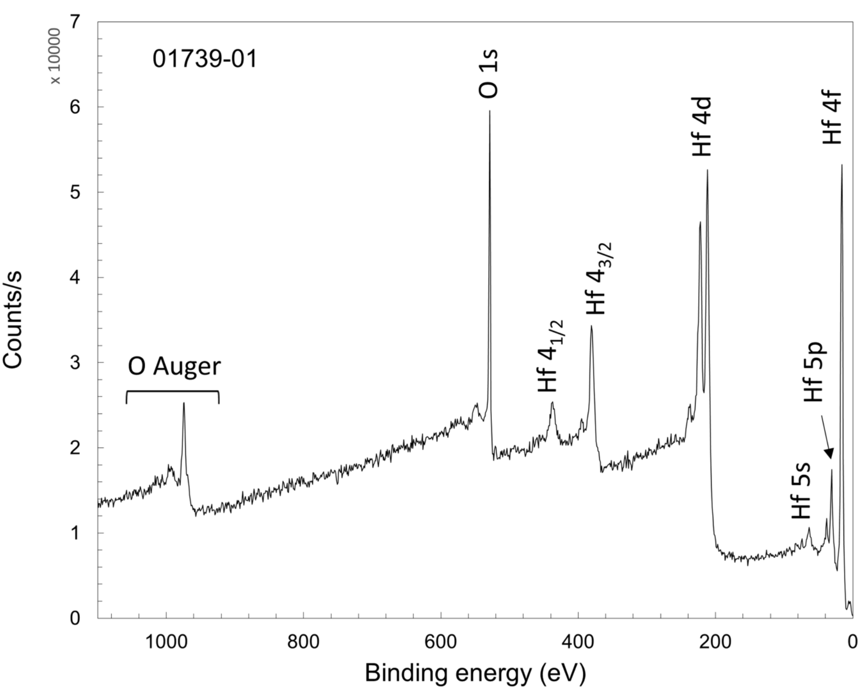

Accession #	01739-01
Host Material:	HfO_2
Technique:	XPS
Spectral Region:	Survey
Instrument:	ULVAC-PHI Quantes
Excitation Source:	Al K_α monochromatic
Source Energy:	1486.6 eV
Source Strength:	25 W
Source Size:	0.1 × 0.1 mm^2
Analyzer Type:	Spherical sector analyzer
Incident Angle:	22°
Emission Angle:	45°
Analyzer Pass Energy:	280 eV
Analyzer Resolution:	1.9 eV
Total Signal Accumulation Time:	110 s
Total Elapsed Time:	130 s
Number of Scans:	1
Effective Detector Width:	31 eV

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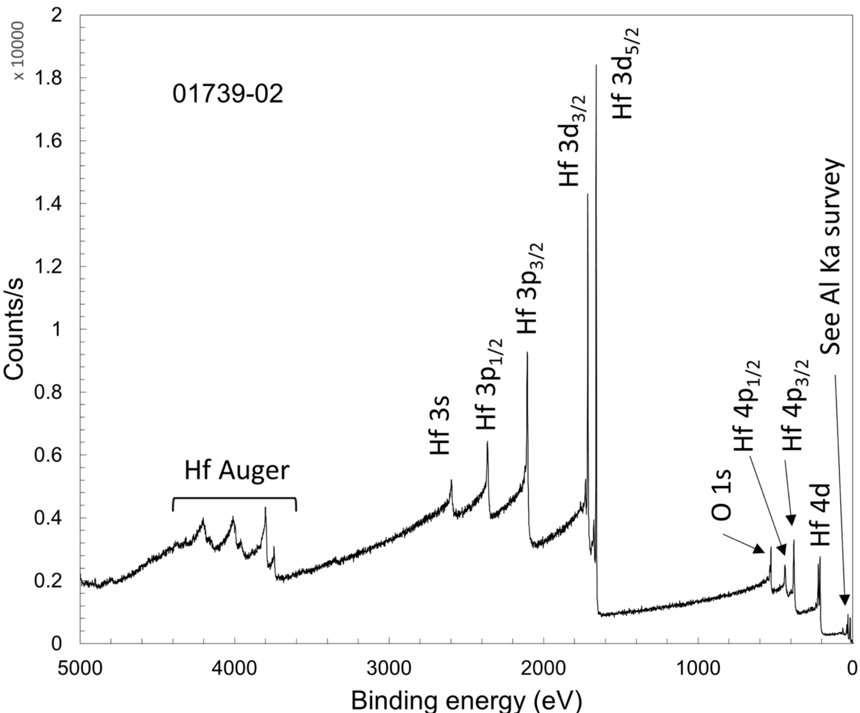

Accession #	01739-02
Host Material:	HfO_2
Technique:	XPS
Spectral Region:	Survey
Instrument:	ULVAC-PHI Quantes
Excitation Source:	Cr K_α monochromatic
Source Energy:	5414.8 eV
Source Strength:	43 W
Source Size:	0.1 × 0.1 mm^2
Analyzer Type:	spherical sector analyzer
Incident Angle:	22°
Emission Angle:	45°
Analyzer Pass Energy:	280 eV
Analyzer Resolution:	1.9 eV
Total Signal Accumulation Time:	2500 s
Total Elapsed Time:	2750 s
Number of Scans:	10
Effective Detector Width:	31 eV

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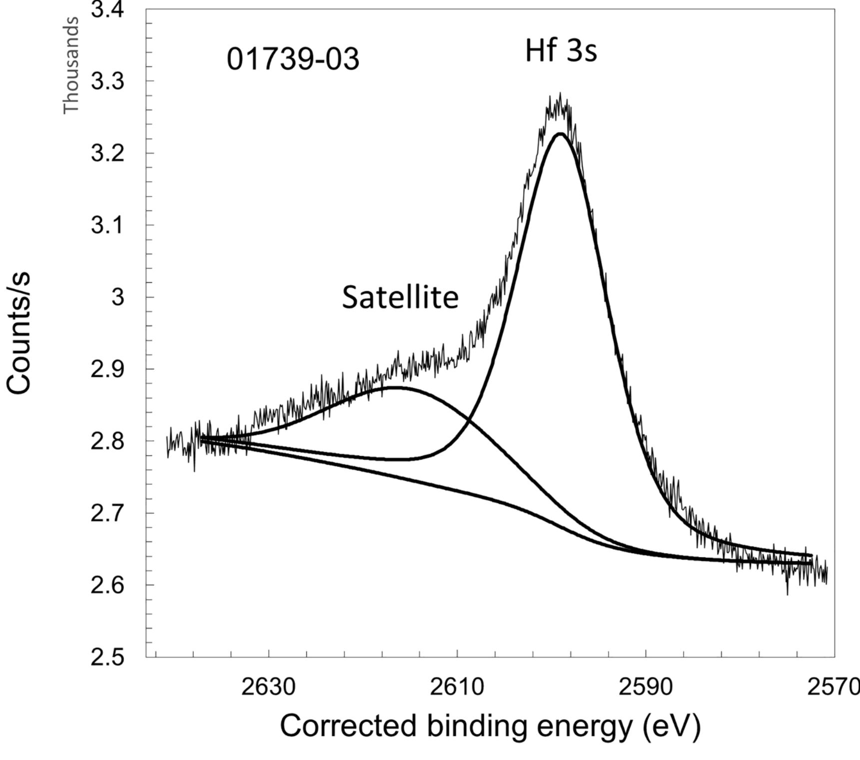
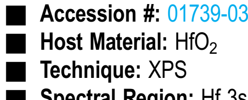
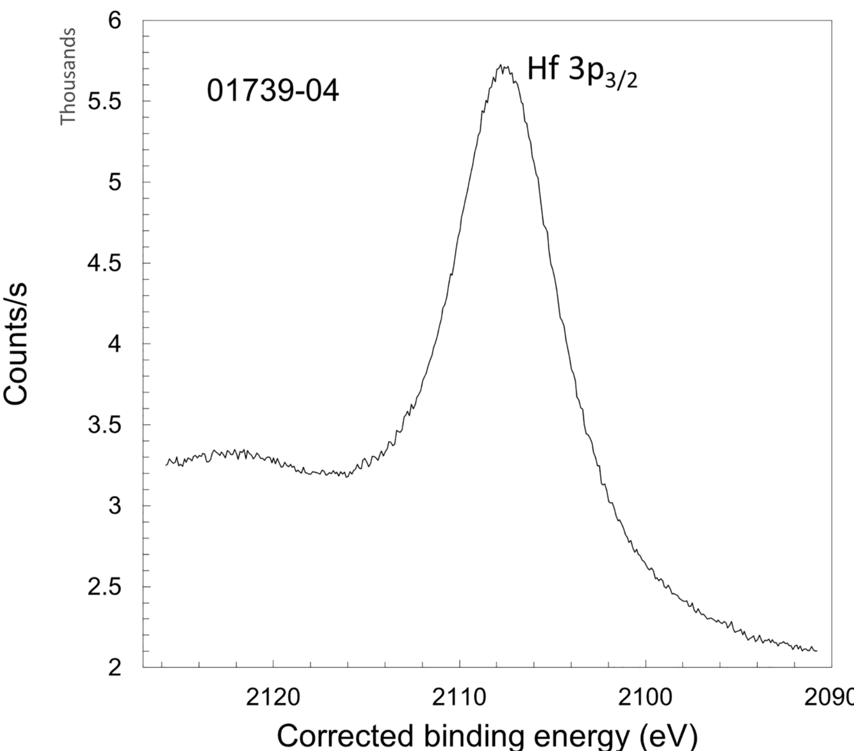
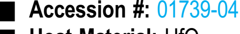




- **Accession #:** 01739-03
- **Host Material:** HfO_2
- **Technique:** XPS
- **Spectral Region:** Hf 3s

Instrument: ULVAC-PHI Quantes
Excitation Source: Cr K_{α} monochromatic
Source Energy: 5414.8 eV
Source Strength: 52 W
Source Size: 0.1 × 0.1 mm^2
Analyzer Type: Spherical sector
Incident Angle: 22°
Emission Angle: 45°
Analyzer Pass Energy: 112 eV
Analyzer Resolution: 0.86 eV
Total Signal Accumulation Time: 11 200 s
Total Elapsed Time: 12 300 s
Number of Scans: 160
Effective Detector Width: 12.4 eV





- **Accession #:** 01739-04
- **Host Material:** HfO_2
- **Technique:** XPS
- **Spectral Region:** Hf $3p_{3/2}$

Instrument: ULVAC-PHI Quantes
Excitation Source: Cr K_{α} monochromatic
Source Energy: 5414.8 eV
Source Strength: 52 W
Source Size: 0.1 × 0.1 mm^2
Analyzer Type: Spherical sector
Incident Angle: 22°
Emission Angle: 45°
Analyzer Pass Energy: 112 eV
Analyzer Resolution: 0.86 eV
Total Signal Accumulation Time: 3650 s
Total Elapsed Time: 4015 s
Number of Scans: 104
Effective Detector Width: 12.4 eV

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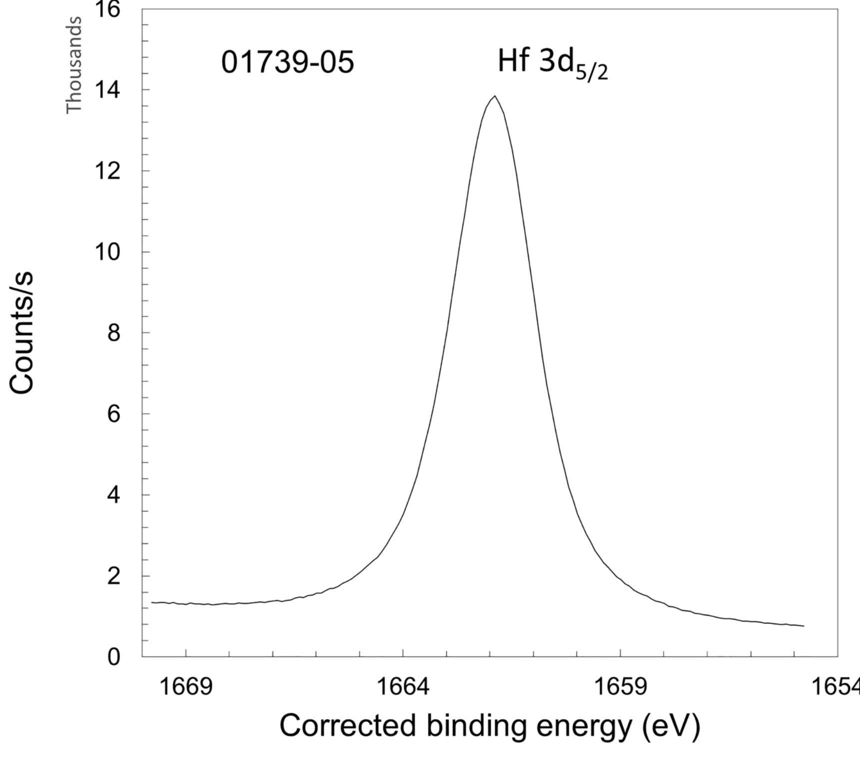
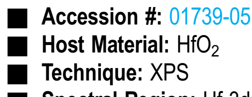
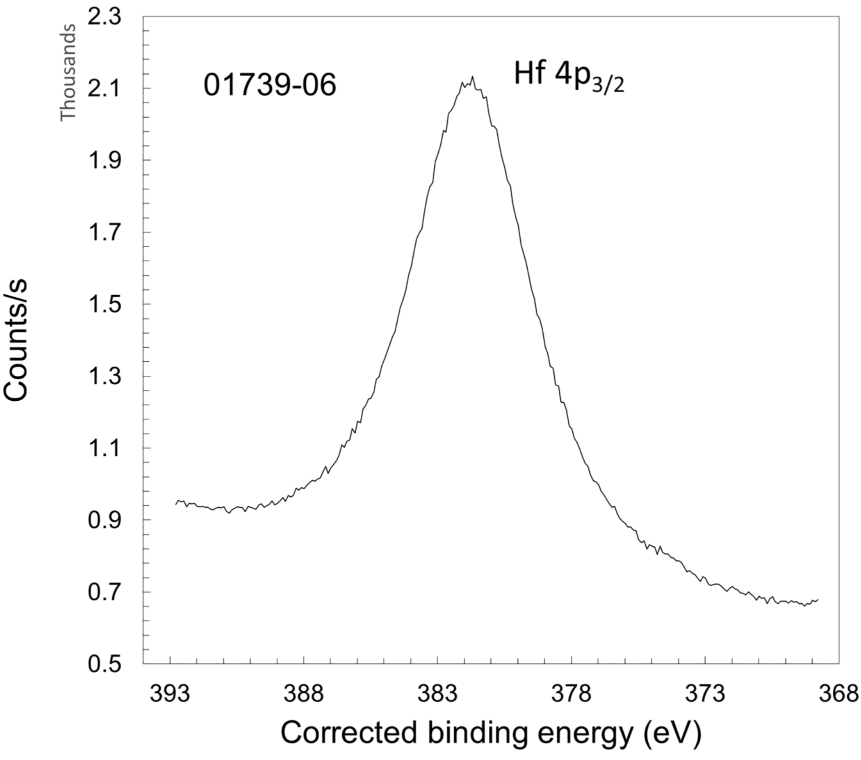




- **Accession #:** 01739-05
- **Host Material:** HfO_2
- **Technique:** XPS
- **Spectral Region:** Hf 3d5/2

Instrument: ULVAC-PHI Quantes
Excitation Source: Cr K_α monochromatic
Source Energy: 5414.8 eV
Source Strength: 52 W
Source Size: 0.1 × 0.1 mm^2
Analyzer Type: Spherical sector
Incident Angle: 22°
Emission Angle: 45°
Analyzer Pass Energy: 112 eV
Analyzer Resolution: 0.86 eV
Total Signal Accumulation Time: 2000 s
Total Elapsed Time: 2200 s
Number of Scans: 132
Effective Detector Width: 12.4 eV



- **Accession #:** 01739-06
- **Host Material:** HfO_2
- **Technique:** XPS
- **Spectral Region:** Hf 4p3/2

Instrument: ULVAC-PHI Quantes
Excitation Source: Cr K_α monochromatic
Source Energy: 5414.8 eV
Source Strength: 52 W
Source Size: 0.1 × 0.1 mm^2
Analyzer Type: Spherical sector
Incident Angle: 22°
Emission Angle: 45°
Analyzer Pass Energy: 112 eV
Analyzer Resolution: 0.86 eV
Total Signal Accumulation Time: 4800 s
Total Elapsed Time: 5300 s
Number of Scans: 200
Effective Detector Width: 12.4 eV

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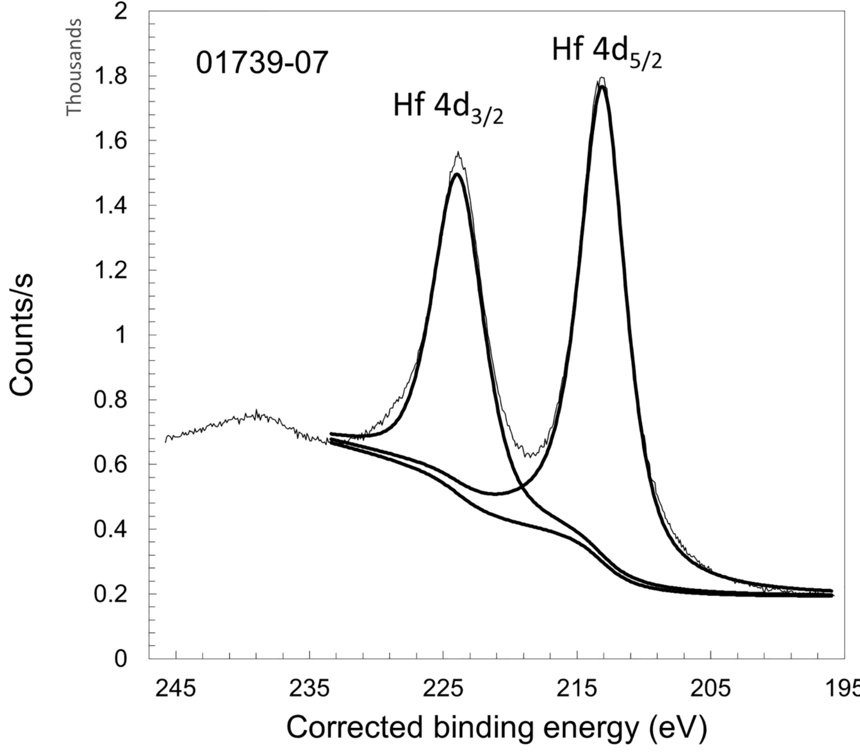
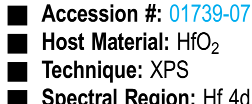
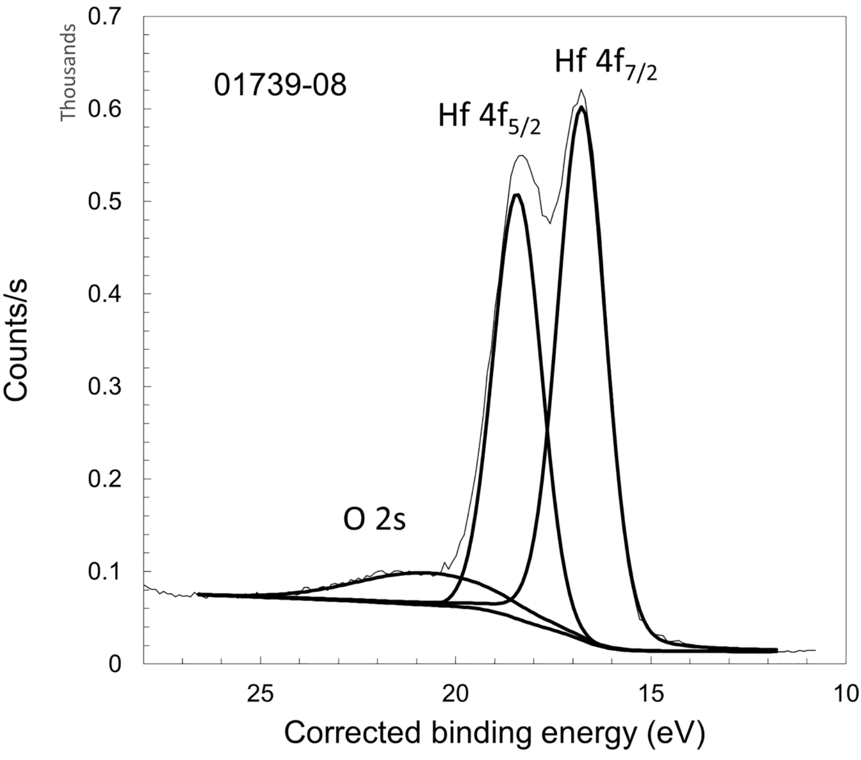




- **Accession #:** 01739-07
- **Host Material:** HfO_2
- **Technique:** XPS
- **Spectral Region:** Hf 4d

Instrument: ULVAC-PHI Quantes
Excitation Source: Cr K_α monochromatic
Source Energy: 5414.8 eV
Source Strength: 52 W
Source Size: 0.1 × 0.1 mm^2
Analyzer Type: Spherical sector
Incident Angle: 22°
Emission Angle: 45°
Analyzer Pass Energy: 112 eV
Analyzer Resolution: 0.86 eV
Total Signal Accumulation Time: 6410 s
Total Elapsed Time: 7050 s
Number of Scans: 160
Effective Detector Width: 12.4 eV



- **Accession #:** 1739-08
- **Host Material:** HfO_2
- **Technique:** XPS
- **Spectral Region:** Hf 4f

Instrument: ULVAC-PHI Quantes
Excitation Source: Cr K_α monochromatic
Source Energy: 5414.8 eV
Source Strength: 52 W
Source Size: 0.1 × 0.1 mm^2
Analyzer Type: Spherical sector
Incident Angle: 22°
Emission Angle: 45°
Analyzer Pass Energy: 112 eV
Analyzer Resolution: 0.86 eV
Total Signal Accumulation Time: 4020 s
Total Elapsed Time: 4420 s
Number of Scans: 200
Effective Detector Width: 12.4 eV

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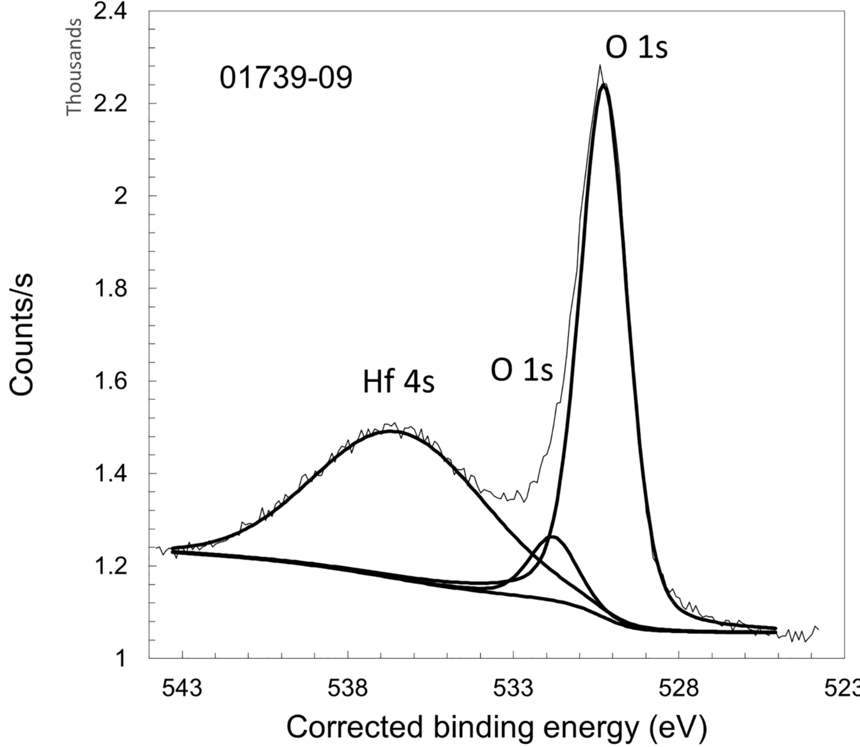

- **Accession #:** 01739-09
- **Host Material:** HfO_2
- **Technique:** XPS
- **Spectral Region:** O 1s

Instrument: ULVAC-PHI Quantes
Excitation Source: Cr K_{α} monochromatic
Source Energy: 5414.8 eV
Source Strength: 52 W
Source Size: 0.1 × 0.1 mm^2
Analyzer Type: Spherical sector
Incident Angle: 22°
Emission Angle: 45°
Analyzer Pass Energy: 112 eV
Analyzer Resolution: 0.86 eV
Total Signal Accumulation Time: 2400 s
Total Elapsed Time: 2650 s
Number of Scans: 120
Effective Detector Width: 12.4 eV

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