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High-energy x-ray photoelectron spectroscopy spectra of TiO_2 measured by $\text{Cr K}\alpha$

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High-energy x-ray photoelectron spectroscopy spectra of TiO₂ measured by Cr K α

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

ABSTRACT

Titanium oxide (TiO₂) grown by physical vapor deposition (PVD) on Si was analyzed using high-resolution high-energy x-ray photoelectron spectroscopy (HAXPES). The HAXPES spectra of TiO₂ obtained using monochromatic Cr K α radiation at 5414.8 eV include two survey scans (Al K α and Cr K α) and high-resolution spectra of Ti 1s, Ti2p, Ti 2s, Ti 3p, Ti 3s, and O 1s.

Key words: TiO₂, HAXPES, Cr K α

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Accession#: 01738 and 01743

Technique: XPS, XAES

Host Material: TiO₂

Instrument: ULVAC-PHI Quantes

Major Elements in Spectra: Ti, O

Minor Elements in Spectra: None

Published Spectra: 9

Spectra in Electronic Record: 9

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 titanium oxide (TiO₂) grown by physical vapor deposition (PVD) on Si, which was analyzed using high-resolution high-energy x-ray photoelectron spectroscopy (HAXPES). The HAXPES spectra of TiO₂ obtained using monochromatic Cr K α radiation at 5414.8 eV include two survey scans (Al K α and Cr K α) and high-resolution spectra of Ti 1s, Ti2p, Ti 2s, Ti 3p, Ti 3s, and O 1s.

SPECIMEN DESCRIPTION (ACCESSION # 01738)

Host Material: TiO₂

CAS Registry #: 13463-67-7

Host Material Characteristics: Homogeneous; solid; amorphous; dielectric; inorganic compound; thin film

Chemical Name: Titanium oxide

Source: PVD grown

Host Composition: Ti, O

Form: Thin film

Structure: Amorphous

History and Significance: Air-exposed PVD TiO₂

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 K α 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 × 10⁻⁷ Pa

Pre-analysis Beam Exposure: 0 s

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 × 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 × 100 μm²
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 K_α, and the presputtering of the sample, the binding energy was referenced by determining the binding energy position of the Ti 2p_{3/2} peak recorded by Al K_α XPS measurement and subsequent correction shift of the C 1s peak to 284.8 eV. The determined binding energy position of the Ti 2p_{3/2} peak is 458.69 eV. The binding energy shift of the Cr K_α data was then performed by shifting the Ti 2p_{3/2} peak to 458.69 eV.

Recommended Energy Scale Shift: 1.17 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(E_p), 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(E_p) = (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<https://www.ulvac-phi.com/en/products/xps/quantes/>.
- ²<https://www.kratos.com/products/axis-supra-xps-surface-analysis-instrument>.
- ³<https://scientaomicron.com/en/system-solutions/electron-spectroscopy/HAXPES-Lab>.
- ⁴See **supplementary material** at <https://doi.org/10.1116/6.0001529> for ASCII data of all shown spectra.

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
01738-03	Ti 1s	4968.95	2.19	9333	2.476	32.2	TiO ₂
01738-04	Ti 2s	565.08	4.59	2117	0.921	30.6	TiO ₂
01738-05 ^b	Ti 2p _{3/2}	458.69	1.52	1759	0.468	40.1	TiO ₂
01738-05	Ti 2p _{1/2}	464.33	2.25	869	0.234	...	TiO ₂
01738-06	Ti 3s	62.11	2.80	462	0.141	39.6	TiO ₂
01738-07	Ti 3p	37.09	2.47	356	0.115	36.8	TiO ₂
01738-08	O 1s	530.07	1.60	2566	0.589	...	TiO ₂

^aThe concentration is calculated by taking into account only the O 1s peak and the Ti peak from the given transition.

^bConcentration quantification based on the full Ti 2p intensity.

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	2 978

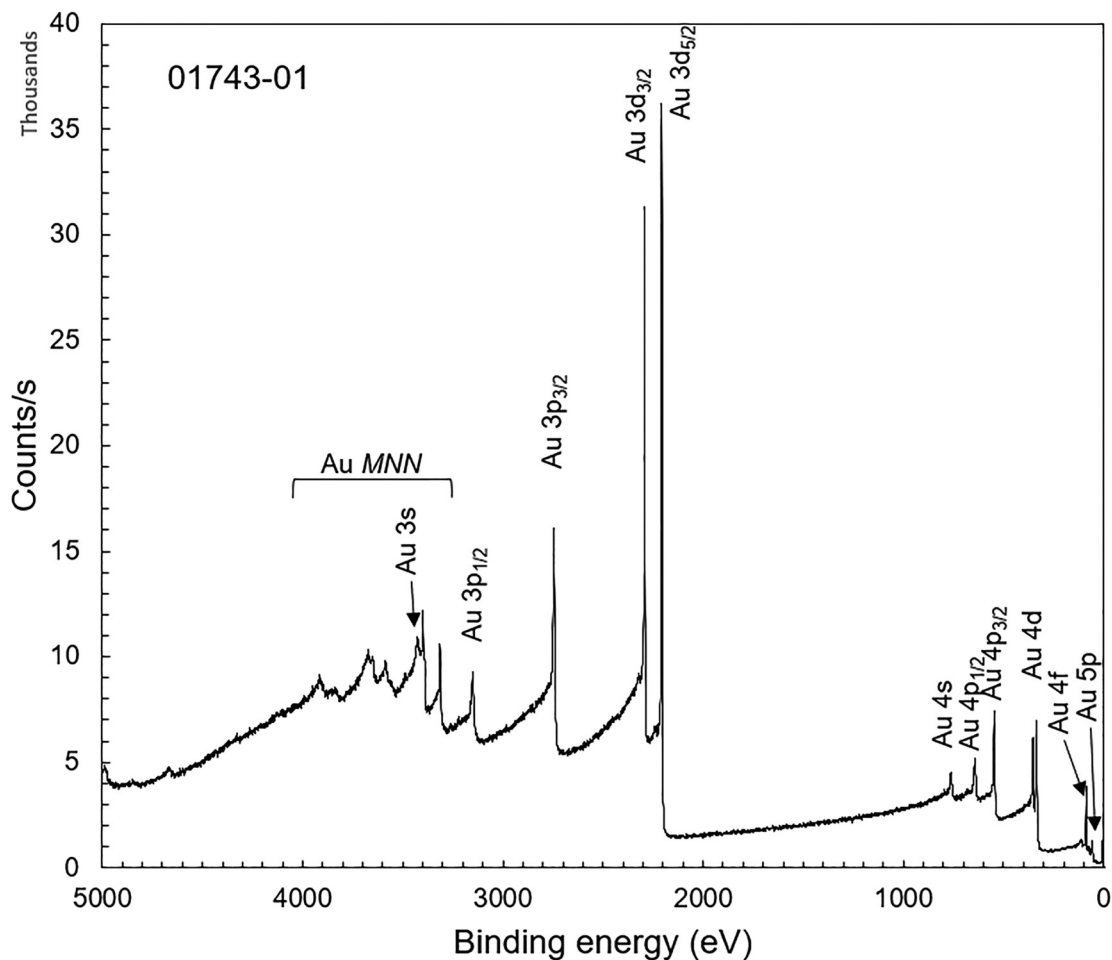
^aThe calibration table is established using the Cr Kα photons and a pass energy of 112 eV corresponding to the presented high-resolution spectra.

GUIDE TO FIGURES

Spectrum (Accession) #	Spectral Region	Voltage Shift ^a	Multiplier	Baseline	Comment #
01743-01	Survey	0	1	0	Au survey with x-ray source Cr Kα ^b
01738-01	Survey	0	1	0	X-ray source Al Kα
01738-02	Survey	0	1	0	X-ray source Cr Kα
01738-03	Ti 1s	-1.17	1	0	...
01738-04	Ti 2s	-1.17	1	0	...
01738-05	Ti 2p	-1.17	1	0	...
01738-06	Ti 3s	-1.17	1	0	...
01738-07	Ti 3p	-1.17	1	0	...
01738-08	O 1s	-1.17	1	0	...

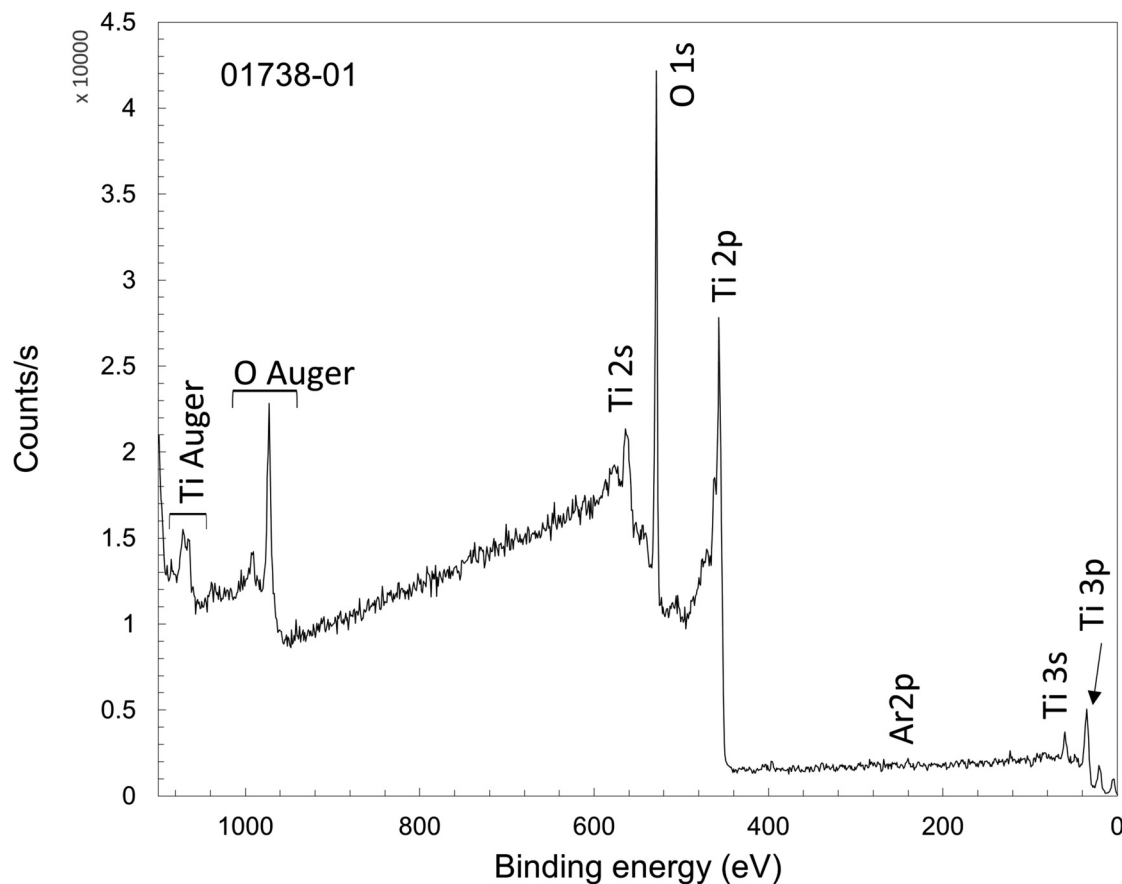
^aVoltage shift of the archived (as-measured) spectrum relative to the printed figure. The figure reflects the recommended energy scale correction due to a calibration correction, sample charging, flood gun, or other phenomenon.

^bThe 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.



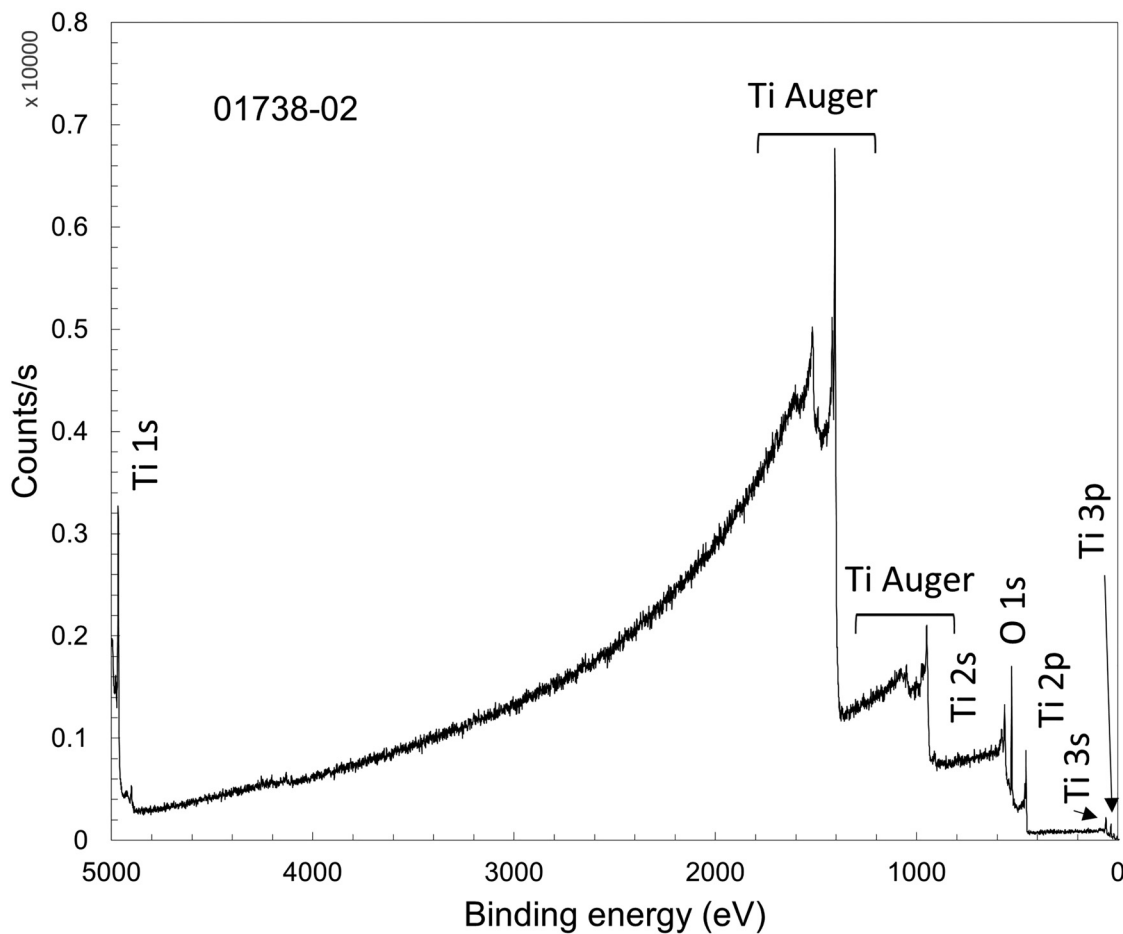
Accession #	01743-01
Host Material:	Au
Technique:	XPS
Spectral Region:	Survey
Instrument:	ULVAC-PHI Quantes
Excitation Source:	Cr K _α monochromatic
Source Energy:	5414.8 eV
Source Strength:	49 W
Source Size:	0.1 × 0.1 mm ²
Analyzer Type:	Spherical sector analyzer
Incident Angle:	22°
Emission Angle:	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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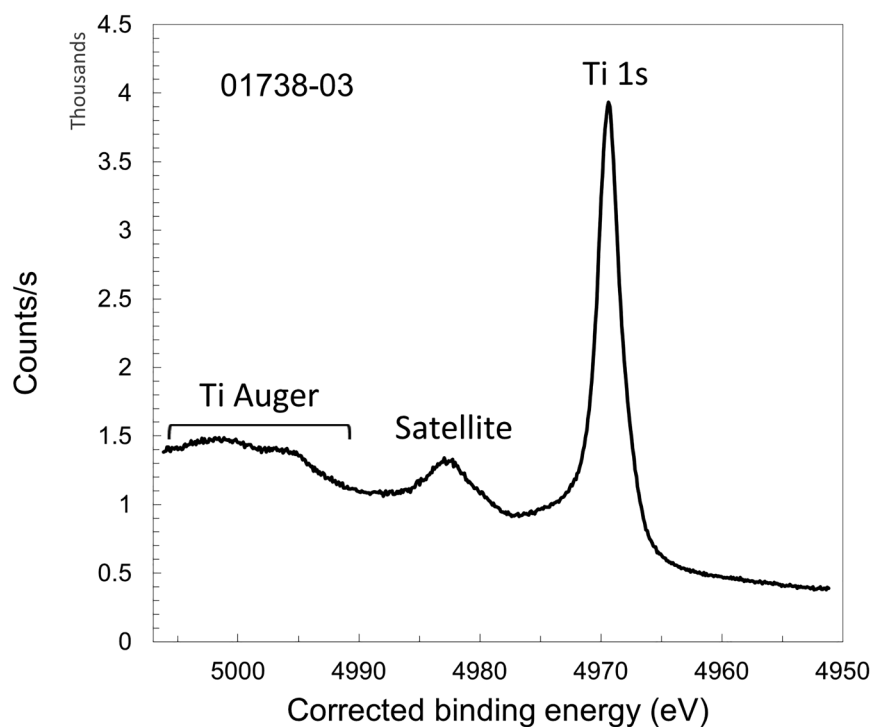
Accession #	01738-01
Host Material:	TiO ₂
Technique:	XPS
Spectral Region:	Survey
Instrument:	ULVAC-PHI Quantes
Excitation Source:	Al K _α monochromatic
Source Energy:	1486.6 eV
Source Strength:	25 W
Source Size:	0.1 × 0.1 mm ²
Analyzer Type:	Spherical sector analyzer
Incident Angle:	22°
Emission Angle:	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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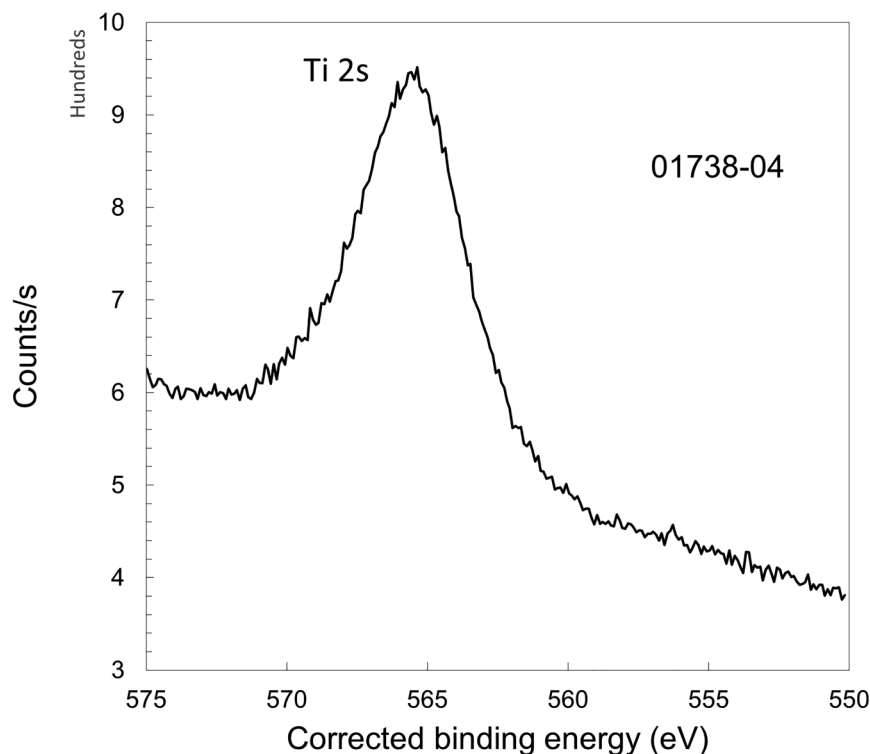
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Accession #	01738-02
Host Material:	TiO ₂
Technique:	XPS
Spectral Region:	Survey
Instrument:	ULVAC-PHI Quantes
Excitation Source:	Cr K _α monochromatic
Source Energy:	5414.8 eV
Source Strength:	43 W
Source Size:	0.1 × 0.1 mm ²
Analyzer Type:	Spherical 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



- Accession #: 01738-03
- Host Material: TiO₂
- Technique: XPS, XAES
- Spectral Region: Ti 1s

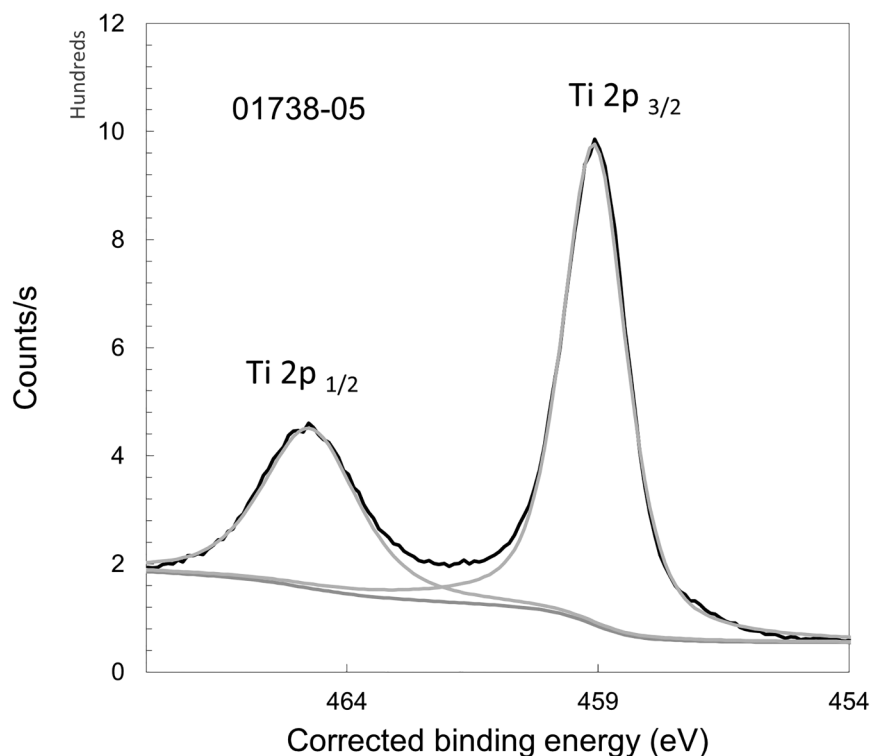
Instrument: ULVAC-PHI Quantes
 Excitation Source: Cr K_α monochromatic
 Source Energy: 5414.8 eV
 Source Strength: 43 W
 Source Size: 0.1 × 0.1 mm²
 Analyzer Type: Spherical sector
 Incident Angle: 22°
 Emission Angle: 45°
 Analyzer Pass Energy: 112 eV
 Analyzer Resolution: 0.86 eV
 Total Signal Accumulation Time: 7700 s
 Total Elapsed Time: 8500 s
 Number of Scans: 140
 Effective Detector Width: 12.4 eV



- Accession #: 01738-04
- Host Material: TiO₂
- Technique: XPS
- Spectral Region: Ti 2s

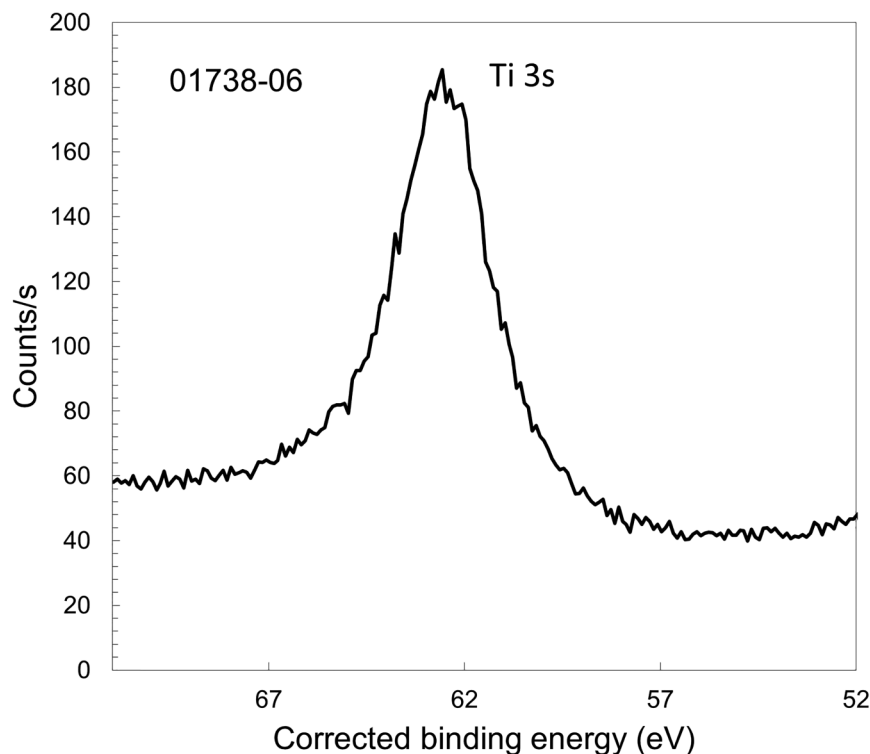
Instrument: ULVAC-PHI Quantes
 Excitation Source: Cr K_α monochromatic
 Source Energy: 5414.8 eV
 Source Strength: 43 W
 Source Size: 0.1 × 0.1 mm²
 Analyzer Type: Spherical sector
 Incident Angle: 22°
 Emission Angle: 45°
 Analyzer Pass Energy: 112 eV
 Analyzer Resolution: 0.86 eV
 Total Signal Accumulation Time: 4910 s
 Total Elapsed Time: 5400 s
 Number of Scans: 140
 Effective Detector Width: 12.4 eV

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- Accession #: [01738-05](#)
- Host Material: TiO₂
- Technique: XPS
- Spectral Region: Ti 2p

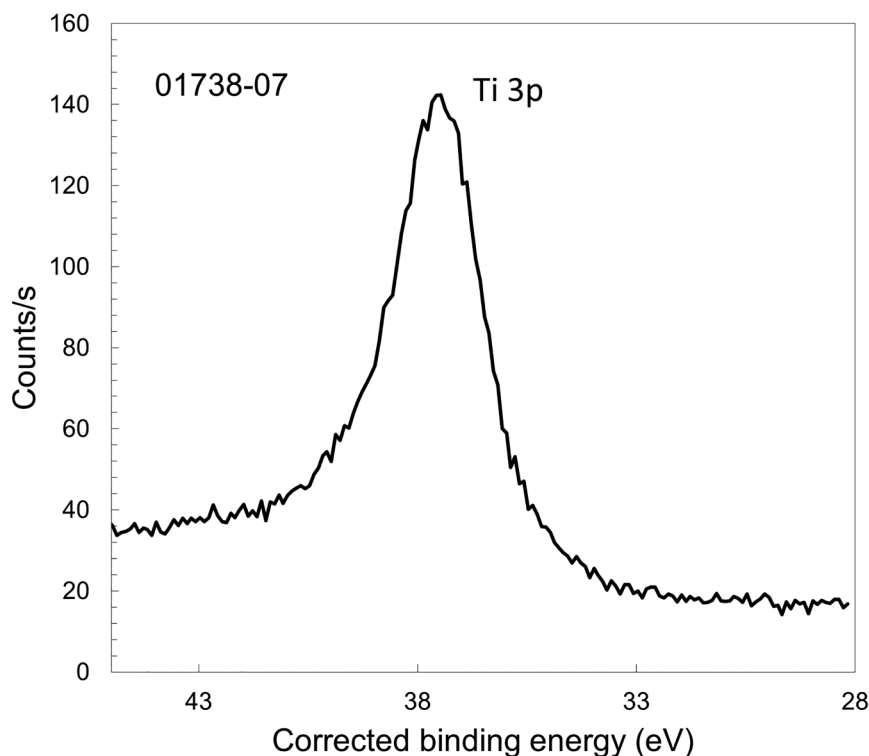
Instrument: ULVAC-PHI Quantes
 Excitation Source: Cr K_α monochromatic
 Source Energy: 5414.8 eV
 Source Strength: 43 W
 Source Size: 0.1 × 0.1 mm²
 Analyzer Type: Spherical sector
 Incident Angle: 22°
 Emission Angle: 45°
 Analyzer Pass Energy: 112 eV
 Analyzer Resolution: 0.86 eV
 Total Signal Accumulation Time: 4500 s
 Total Elapsed Time: 5000 s
 Number of Scans: 180
 Effective Detector Width: 12.4 eV



- Accession #: [01738-06](#)
- Host Material: TiO₂
- Technique: XPS
- Spectral Region: Ti 3s

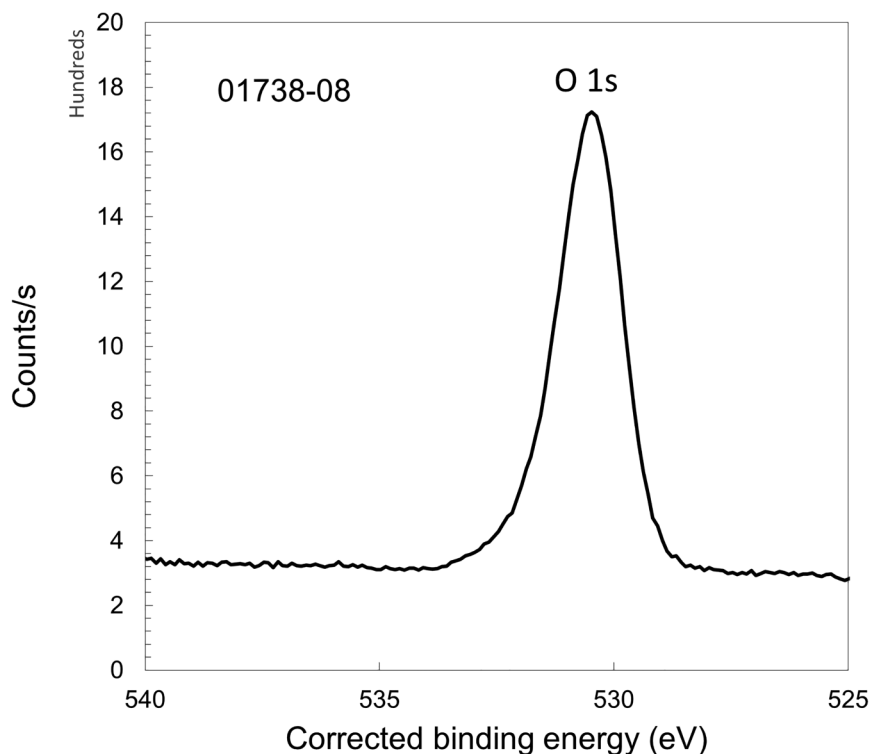
Instrument: ULVAC-PHI Quantes
 Excitation Source: Cr K_α monochromatic
 Source Energy: 5414.8 eV
 Source Strength: 43 W
 Source Size: 0.1 × 0.1 mm²
 Analyzer Type: Spherical sector
 Incident Angle: 22°
 Emission Angle: 45°
 Analyzer Pass Energy: 112 eV
 Analyzer Resolution: 0.86 eV
 Total Signal Accumulation Time: 4000 s
 Total Elapsed Time: 4400 s
 Number of Scans: 200
 Effective Detector Width: 12.4 eV

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- Accession #: 01738-07
- Host Material: TiO₂
- Technique: XPS
- Spectral Region: Ti 3p

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 mm²
 Analyzer Type: Spherical sector
 Incident Angle: 22°
 Emission Angle: 45°
 Analyzer Pass Energy: 112 eV
 Analyzer Resolution: 0.86 eV
 Total Signal Accumulation Time: 3600 s
 Total Elapsed Time: 4000 s
 Number of Scans: 200
 Effective Detector Width: 12.4 eV



- Accession #: 01738-08
- Host Material: TiO₂
- Technique: XPS
- Spectral Region: O 1s

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 mm²
 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: 140
 Effective Detector Width: 12.4 eV

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