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

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High-energy x-ray photoelectron spectroscopy spectra of TiN 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 nitride (TiN) grown by ionized metal plasma on Si was analyzed using high-resolution high-energy x-ray photoelectron spectroscopy (HAXPES). The HAXPES spectra of TiN 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, N 1s, and O 1s.

Key words: TiN, HAXPES, Cr K α

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Accession #: 01737 and 01743

Technique: XPS, XAES

Host Material: TiN

Instrument: ULVAC-PHI Quantes

Major Elements in Spectra: Ti, N

Minor Elements in Spectra: O

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.

The samples being air-exposed, a sputter step has been introduced to remove the native oxide. This will lead to nitrogen preferential sputtering and modifications of the final-state orbital screening (Refs. 4 and 5). Thanks to the larger analysis depth of high-energy x-ray photoelectron spectroscopy (HAXPES), this preferential sputtering is not measurable (see spectral figure table) however, as orbital screening occurs at the topmost surface, it may still lead to the reduction of the intensity of the satellite structure observed on the Ti spectra compared to spectra obtained on *in situ* grown materials.

In this work, we present reference spectra from titanium nitride (TiN) grown by ionized metal plasma (IMP) on Si, which was analyzed using high-resolution HAXPES. The HAXPES spectra of TiN 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, N 1s, and O 1s.

SPECIMEN DESCRIPTION (ACCESSION # 01737)

Host Material: TiN

CAS Registry #: 25583-20-4

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

Chemical Name: Titanium nitride

Source: IMP grown

Host Composition: Ti, N

Form: Thin film

Structure: Amorphous

History and Significance: Air-exposed and sputtered IMP TiN. Films were grown at 350 °C and a substrate bias of –221 V.1

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. A subsequent Ar⁺ sputtering with 1.0 keV ions was performed to remove the native oxide.

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

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: $100 \times 100 \mu\text{m}^2$

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° \times 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 N 1s 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 N 1s peak is 396.73 eV. The binding energy shift of the Cr K α data was then performed by shifting the N 1s peak to 396.73 eV.

Recommended Energy Scale Shift: 1.24 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 $Si(\text{ref})$ for the selected element and a measurement of the peak intensity for the selected key material, $I(\text{key})$, as given in Formula (A.7): $Si(E_p) = (I(\text{ref})/I(\text{key}))$.”

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. 6).

REFERENCES

¹See: <https://www.ulvac-phi.com/en/products/xps/quantas/>.

²See: <https://www.kratos.com/products/axis-supra-xps-surface-analysis-instrument>.

³See: <https://scientaomicron.com/en/system-solutions/electron-spectroscopy/HAXPES-Lab>.

⁴R. T. Haasch, J. Patscheider, N. Hellgren, I. Petrov, and J. E. Greene, *Surf. Sci. Spectra* **19**, 33–41 (2012).

⁵R. T. Haasch, J. Patscheider, N. Hellgren, I. Petrov, and J. E. Greene, *Surf. Sci. Spectra* **19**, 92–97 (2012).

⁶See supplementary material at <https://doi.org/10.1116/6.0001528> for ASCII data of all shown spectra is available.

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
01737-03	Ti 1s	4965.35	3.37	11 825	2.476	48.3	TiN
01737-04	Ti 2s	561.94	591	2926	0.921	49.0	TiN
01737-05 ^b	Ti 2p _{3/2}	454.54	...	2982	0.702	55.1	TiN
01737-05	Ti 2p _{1/2}	460.58	TiN
01737-06	Ti 3s	59.34	4.49	637	0.141	59.5	TiN
01737-07	Ti 3p	34.67	4.44	414	0.115	51.5	TiN
01737-08	O 1s	530.2	2.5	93
01737-09	N 1s	396.80	1.55	911	TiN

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

^bPeak area—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	2115
...	Cu 2p _{3/2}	932.9	1.34	7090
...	Ag 2p _{3/2}	3352.7	2.61	30 352
...	Ag 3d _{5/2}	368.4	1.15	2978

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

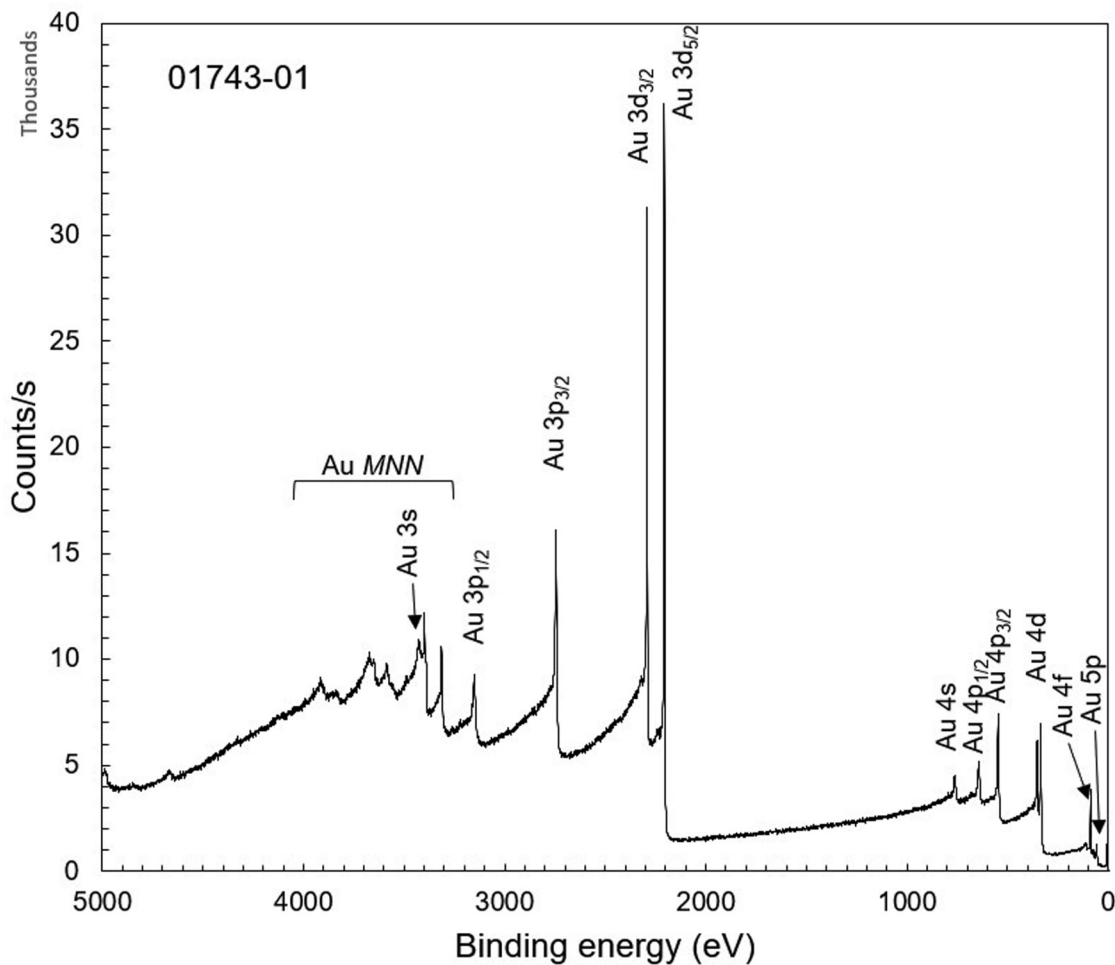
GUIDE TO FIGURES

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
01737-01	Survey	0	1	0	X-ray source Al Kα
01737-02	Survey	0	1	0	X-ray source Cr Kα
01737-03	Ti 1s	-1.24	1	0	...
01737-04	Ti 2s	-1.24	1	0	...
01737-05	Ti 2p	-1.24	1	0	...
01737-06	Ti 3s	-1.24	1	0	...
01737-07	Ti 3p	-1.24	1	0	Data spikes have been removed
01737-08	O 1s	-1.24	1	0	...
01737-09	N 1s	-1.24	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.

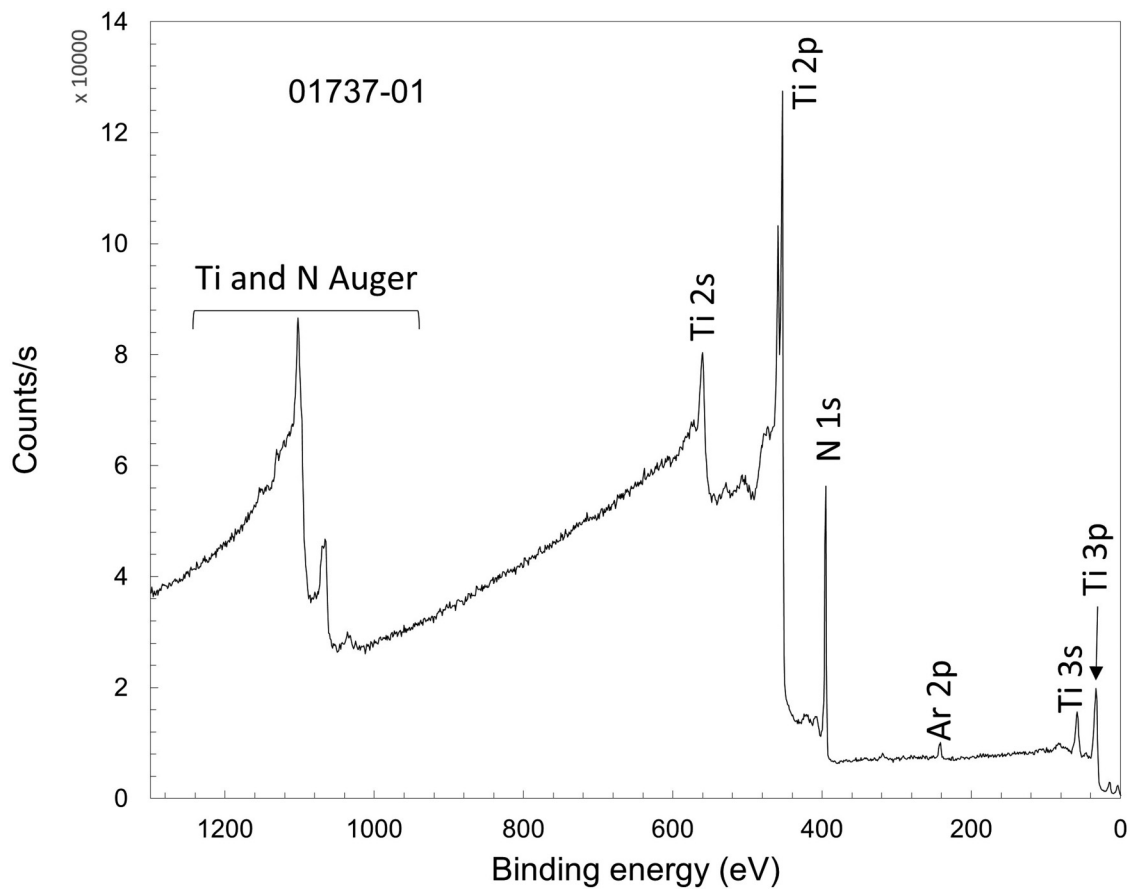
^bThe reference spectrum included in this paper is the same as those included with other papers in this collection that use this x-ray source. This was intentional and not an error as submissions were requested to be accompanied by a wide-scan spectrum of sputter-cleaned gold taken on the same instrument and using the same settings as the wide-scan spectrum of the material or materials in the submission.

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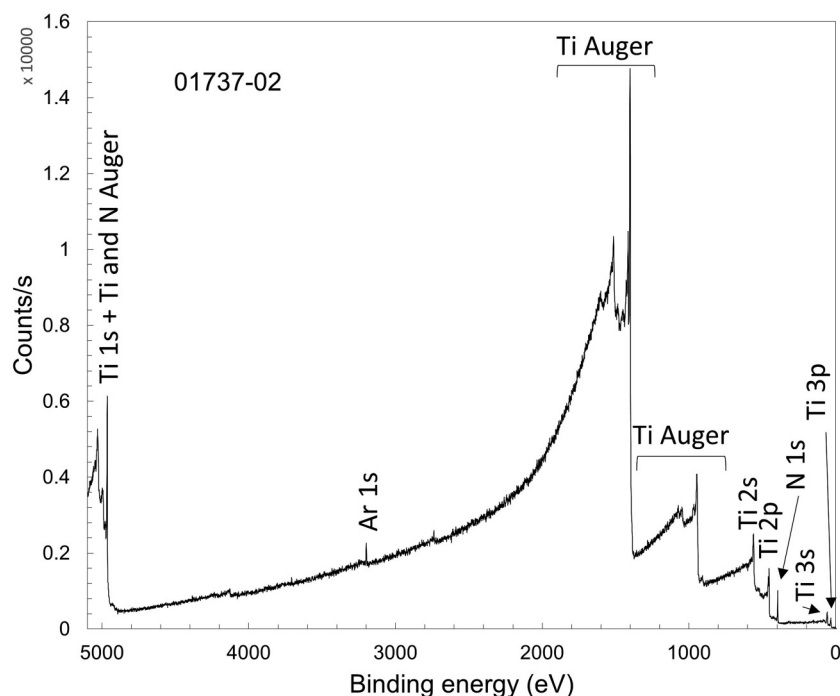
Accession #	01743-01
Host Material:	Au
Technique:	XPS
Spectral Region:	Survey
Instrument:	ULVAC-PHI Quantes
Excitation Source:	Cr K _α monochromatic
Source Energy:	5414.8 eV
Source Strength:	49 W
Source Size:	0.1 × 0.1 mm ²
Analyzer Type:	Spherical sector analyzer
Incident Angle:	22°
Emission Angle:	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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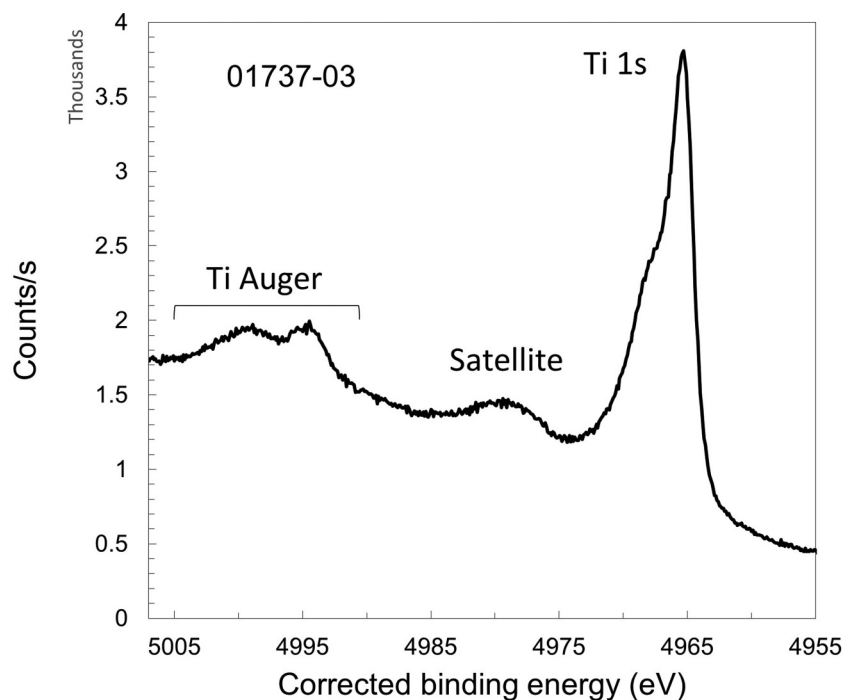
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Accession #:	01737-01
Host Material:	TiN
Technique:	XPS
Spectral Region:	Survey
Instrument:	ULVAC-PHI Quantes
Excitation Source:	Al K α monochromatic
Source Energy:	1486.6 eV
Source Strength:	25 W
Source Size:	0.1 \times 0.1 mm ²
Analyzer Type:	Spherical 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



- Accession #: [01737-02](#)
- Host Material: TiN
- Technique: XPS
- Spectral Region: Survey

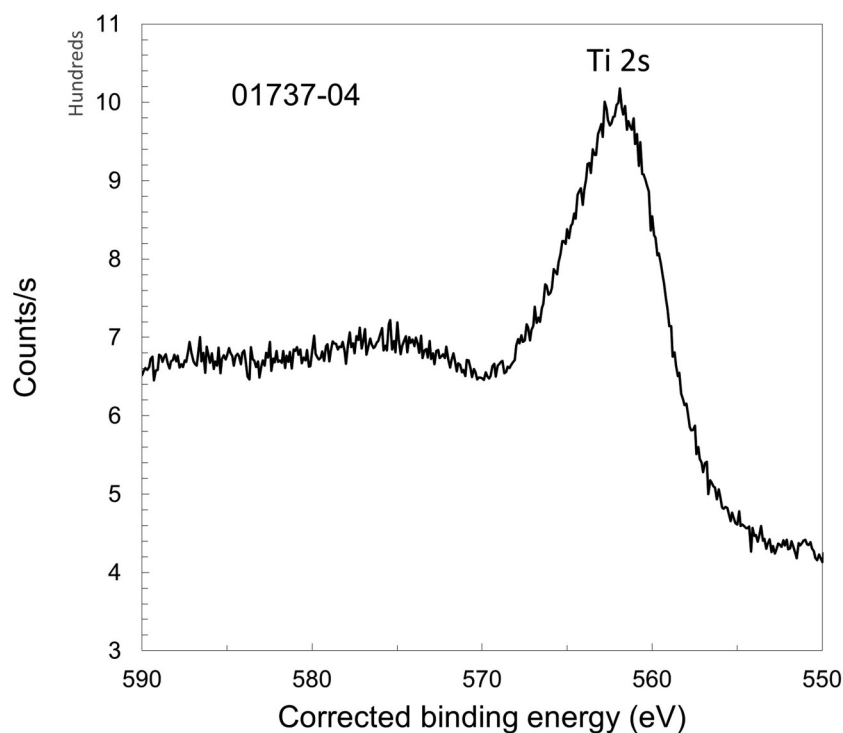
Instrument: ULVAC-PHI Quantes
 Excitation Source: Cr K_{α} monochromatic
 Source Energy: 5414.8 eV
 Source Strength: 43 W
 Source Size: $0.1 \times 0.1 \text{ mm}^2$
 Analyzer Type: Spherical sector analyzer
 Incident Angle: 22°
 Emission Angle: 45°
 Analyzer Pass Energy: 280 eV
 Analyzer Resolution: 1.9 eV
 Total Signal Accumulation Time: 5400 s
 Total Elapsed Time: 6000
 Number of Scans: 10
 Effective Detector Width: 31 eV



- Accession #: [01737-03](#)
- Host Material: TiN
- Technique: XPS, XAES
- Spectral Region: Ti 1s

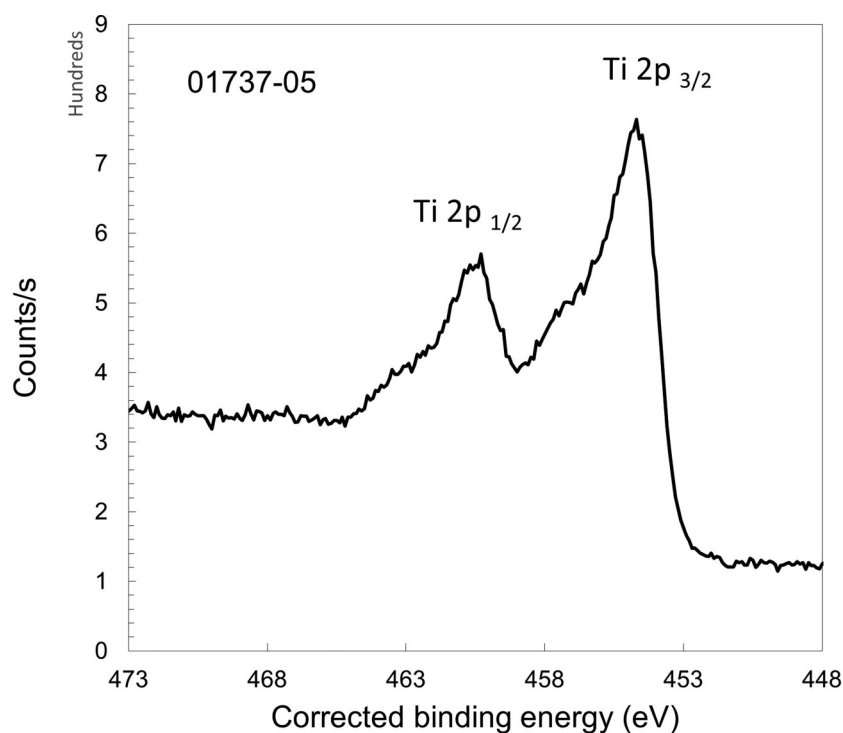
Instrument: ULVAC-PHI Quantes
 Excitation Source: Cr K_{α} monochromatic
 Source Energy: 5414.8 eV
 Source Strength: 43 W
 Source Size: $0.1 \times 0.1 \text{ mm}^2$
 Analyzer Type: Spherical sector
 Incident Angle: 22°
 Emission Angle: 45°
 Analyzer Pass Energy: 112 eV
 Analyzer Resolution: 0.86 eV
 Total Signal Accumulation Time: 4200 s
 Total Elapsed Time: 4620 s
 Number of Scans: 70
 Effective Detector Width: 12.4 eV

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- Accession #: 01737-04
- Host Material: TiN
- Technique: XPS
- Spectral Region: Ti 2s

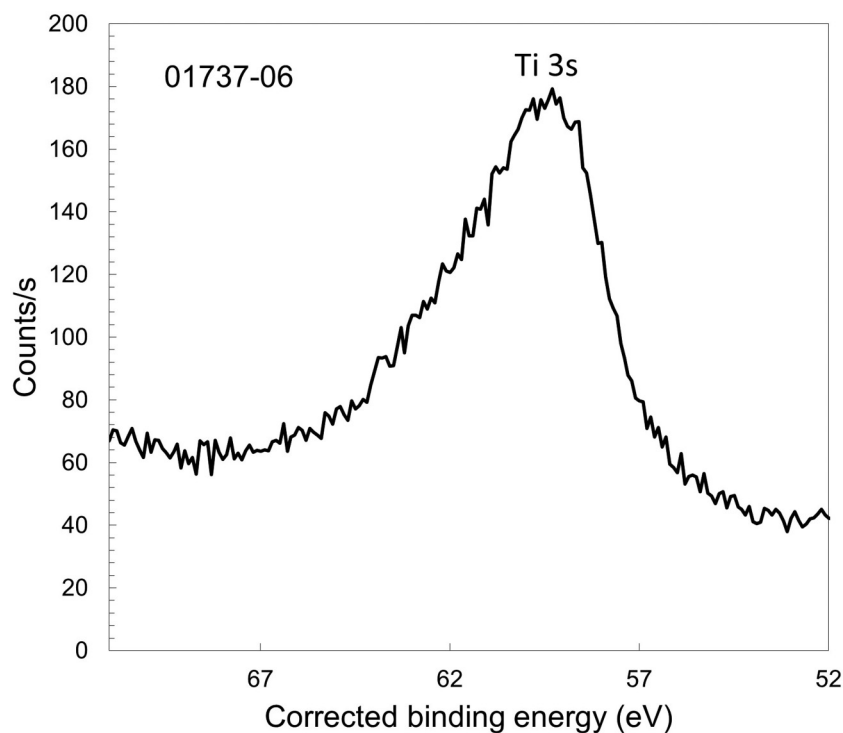
Instrument: ULVAC-PHI Quantes
 Excitation Source: Cr K_{α} monochromatic
 Source Energy: 5414.8 eV
 Source Strength: 43 W
 Source Size: $0.1 \times 0.1 \text{ mm}^2$
 Analyzer Type: Spherical sector
 Incident Angle: 22°
 Emission Angle: 45°
 Analyzer Pass Energy: 112 eV
 Analyzer Resolution: 0.86 eV
 Total Signal Accumulation Time: 3150 s
 Total Elapsed Time: 3500 s
 Number of Scans: 70
 Effective Detector Width: 12.4 eV



- Accession #: 01737-05
- Host Material: TiN
- Technique: XPS
- Spectral Region: Ti 2p

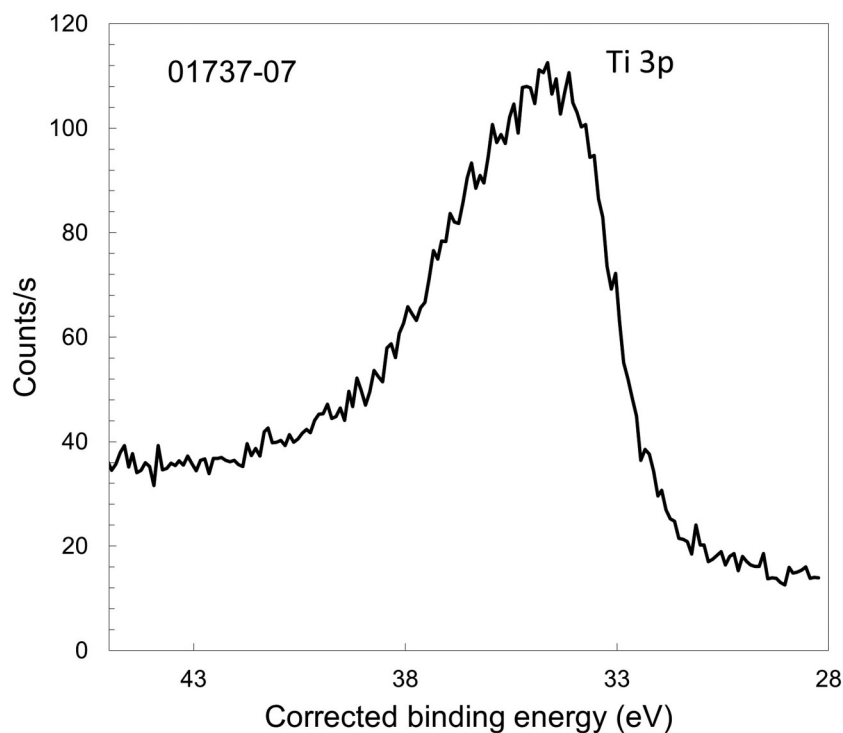
Instrument: ULVAC-PHI Quantes
 Excitation Source: Cr K_{α} monochromatic
 Source Energy: 5414.8 eV
 Source Strength: 43 W
 Source Size: $0.1 \times 0.1 \text{ mm}^2$
 Analyzer Type: Spherical sector
 Incident Angle: 22°
 Emission Angle: 45°
 Analyzer Pass Energy: 112 eV
 Analyzer Resolution: 0.86 eV
 Total Signal Accumulation Time: 2700 s
 Total Elapsed Time: 3000 s
 Number of Scans: 90
 Effective Detector Width: 12.4 eV

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- Accession #: 01737-06
- Host Material: TiN
- Technique: XPS
- Spectral Region: Ti 3s

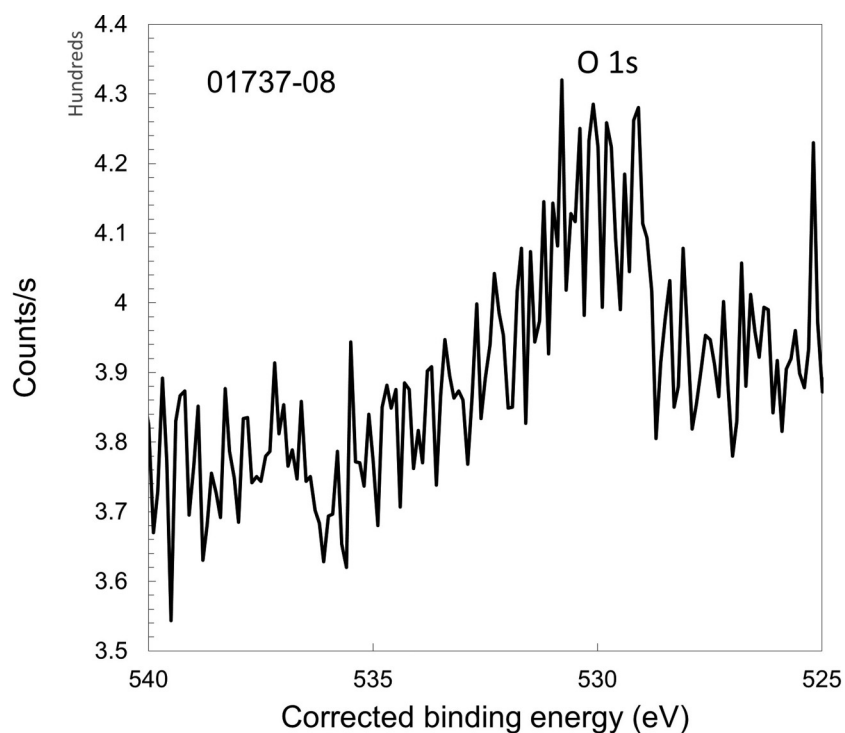
Instrument: ULVAC-PHI Quantes
 Excitation Source: Cr K_{α} monochromatic
 Source Energy: 5414.8 eV
 Source Strength: 43 W
 Source Size: $0.1 \times 0.1 \text{ mm}^2$
 Analyzer Type: Spherical sector
 Incident Angle: 22°
 Emission Angle: 45°
 Analyzer Pass Energy: 112 eV
 Analyzer Resolution: 0.86 eV
 Total Signal Accumulation Time: 2700 s
 Total Elapsed Time: 3000 s
 Number of Scans: 100
 Effective Detector Width: 12.4 eV



- Accession #: 01737-07
- Host Material: TiN
- Technique: XPS
- Spectral Region: Ti 3p

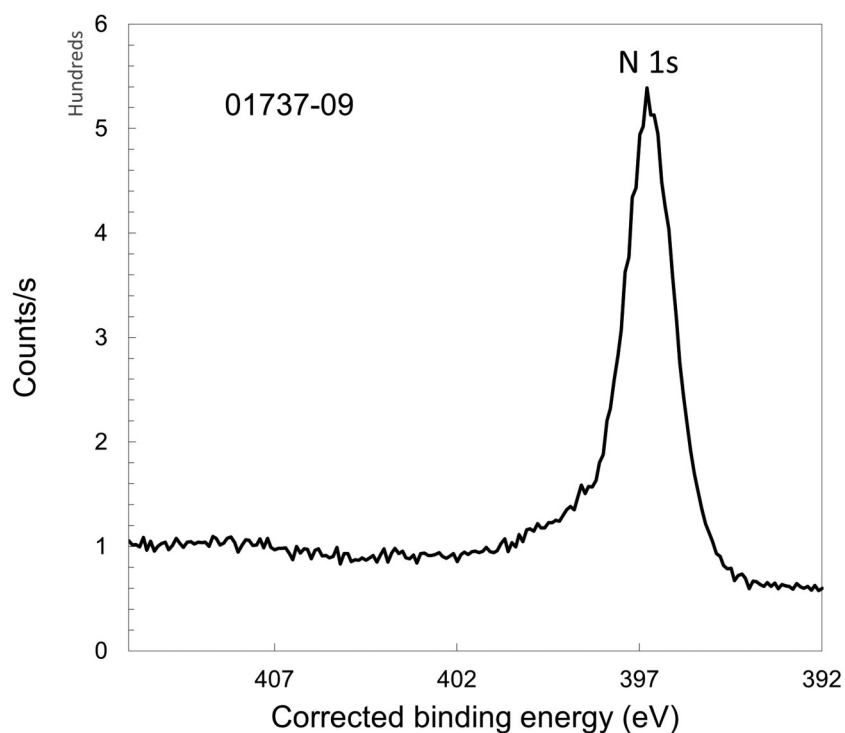
Instrument: ULVAC-PHI Quantes
 Excitation Source: Cr K_{α} monochromatic
 Source Energy: 5414.8 eV
 Source Strength: 43 W
 Source Size: $0.1 \times 0.1 \text{ mm}^2$
 Analyzer Type: Spherical sector
 Incident Angle: 22°
 Emission Angle: 45°
 Analyzer Pass Energy: 112 eV
 Analyzer Resolution: 0.86 eV
 Total Signal Accumulation Time: 1800 s
 Total Elapsed Time: 2100 s
 Number of Scans: 100
 Effective Detector Width: 12.4 eV

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■ **Accession #:** 01737-08
 ■ **Host Material:** TiN
 ■ **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: 1200 s
 Total Elapsed Time: 1350 s
 Number of Scans: 60
 Effective Detector Width: 12.4 eV



■ **Accession #:** 01737-09
 ■ **Host Material:** TiN
 ■ **Technique:** XPS
 ■ **Spectral Region:** N 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: 1200 s
 Total Elapsed Time: 1500 s
 Number of Scans: 200
 Effective Detector Width: 12.4 eV

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