

A Mineral TiO₂(001) Anatase Crystal Examined by XPS

Geert Silversmit, Geert De Doncker, and Roger De Gryse

Department Solid State Sciences, Ghent University, Krijgslaan 281 S1, B-9000 Ghent, Belgium

(Received 8 July 2002; accepted 6 December 2002; published 22 May 2003)

X-ray photoelectron spectroscopy measurements with Al K_{α} radiation of the Ti $2p$, Ti $3p$, O $1s$, and O $2s$ core levels of a mineral anatase TiO₂(001) crystal are presented. The weak Ti $3p$ and O $2s$ photopeaks were measured with two resolutions. The valence band is also presented. © 2003 American Vacuum Society. [DOI: 10.1116/11.20020701]

Keywords: titanium oxide; anatase; TiO₂; photoemission

PACS: 79.60.Bm, 82.80.Pv, 91.60.Ed

Accession # 00745

Technique: XPS

Host Material: TiO₂(001) anatase crystal

Instrument: Physical Electronics, Inc. 5500

Major Elements in Spectrum: Ti, O

Minor Elements in Spectrum: C

Printed Spectra: 10

Spectra in Electronic Record: 13

Spectral Category: technical

SPECIMEN DESCRIPTION

Host Material: TiO₂ (001) anatase crystal

CAS Registry #: 13463-67-7

Host Material Characteristics: homogeneous; solid; single crystal; dielectric; inorganic compound

Chemical Name: titanium (IV) oxide

Source: mineral single crystals found in glacier valleys in Hardangervidda (Norway)

Host Composition: TiO₂

Form: single crystal, (001) plane, anatase polymorph, black in color

Structure: tetragonal, space group 136, (001) plane, $a=b=3.78$ Å, $c=9.51$ Å

History & Significance: Black mineral TiO₂ anatase crystal can be found in Hardangervidda (Norway). The black color is due to contaminations in the mineral (K, Si, Na). Interest: the TiO₂ anatase acts as a support for supported vanadium oxide layers in catalysis.

As Received Condition: See History & Significance

Analyzed Region: host material

Ex Situ Preparation/Mounting: The mineral TiO₂ anatase crystal was oriented to the (001) plane with Laue diffraction. Slices of the crystal were sawn parallel to the (001) plane, polished and etched. Cycles of Ar bombardment at RT and annealing in O₂ at 350 °C were performed to clean the crystal surface. The sample was then transported in air to the ESCA system. More details can be found in Ref. 1.

In Situ Preparation: none

Charge Control: neutralizer model 04-090, electron energy 1 eV, target bias 0 V, filament 3 V and 3.5 A

Temp. During Analysis: 295 K

Pressure During Analysis: $<2 \times 10^{-7}$ Pa

INSTRUMENT DESCRIPTION

Manufacturer and Model: Physical Electronics, Inc. 5500

Analyzer Type: spherical sector

Detector: multichannel detector

Number of Detector Elements: 16

Deviations from Standard Analyzer or Lens: Omni Focus III

INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA

■ Spectrometer

Analyzer Mode: constant pass energy

Throughput ($T=E^N$): $N=0$

Excitation Source Window: none

Excitation Source: Al K_{α} monochromatic

Source Energy: 1486.6 eV

Analyzer Width: 400 $\mu\text{m} \times 400 \mu\text{m}$

Signal Mode: multichannel direct

■ Geometry

Incident Angle: 45°

Source to Analyzer Angle: 90°

Emission Angle: 45°

Specimen Azimuthal Angle: not specified

Acceptance Angle from Analyzer Axis: 7°

Analyzer Angular Acceptance Width: 14° \times 14°

DATA ANALYSIS METHOD

Energy Scale Correction: C 1s taken at 284.6 eV

Recommended Energy-Scale Shift: for Accession #s 745-01 to 07, -1.30 eV; for Accession #s 745-08 to 10, -0.97 eV; no corrections for the calibration spectra

Peak Shape and Background Method: Background is subtracted with a Shirley function. The photopeaks were fitted with mixed Gaussian–Lorentzian curves with no asymmetry.

Quantitation Method: The sensitivity factors were taken from the “PHI Sensitivity Factors Reference Table” of the Physical Electronics standard software. The peak areas are the areas of the fitted curves above the Shirley background. The atomic concentration for an element X is calculated as: $AC(X) = [I_x/S_x]/[\sum I_y/S_y]$, with S_x the sensitivity factor for element X and I_x the area of the fitted Lorentzian–Gaussian curve for the corresponding photopeak of element X.

ACKNOWLEDGMENTS

This work was supported by the Fund for Scientific Research-Flanders (FWO Vlaanderen) and the Belgian Program on the Interuniversity Poles of Attraction.

REFERENCES

1. G. Silversmit, H. Poelman, L. Fiermans, and R. De Gryse, Solid. State Commun. **119**, 101 (2001).

SPECTRAL FEATURES TABLE

Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (cts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
00745-02	O 1s	529.41	1.03	3450	0.711	47.06	...
00745-03	Ti 2p _{3/2}	458.15	0.89	1853	1.198	15.00	...
00745-04	C 1s	284.6	1.16	1158	0.296	37.94	...
00745-05	Ti 3s	61.49	2.37	226
00745-06	Ti 3p	36.48	1.73	456
00745-07	O 2s	21.48	2.1	114
00745-08	Ti 3p	36.87	1.89	1771
00745-09	O 2s	21.88	2.43	575

ANALYZER CALIBRATION TABLE

Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (cts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
11	Au 4f _{7/2}	84.20	0.66	12481
12	Ag 3d _{5/2}	368.47	0.54	14462
13	Cu 2p _{3/2}	932.80	0.85	7645

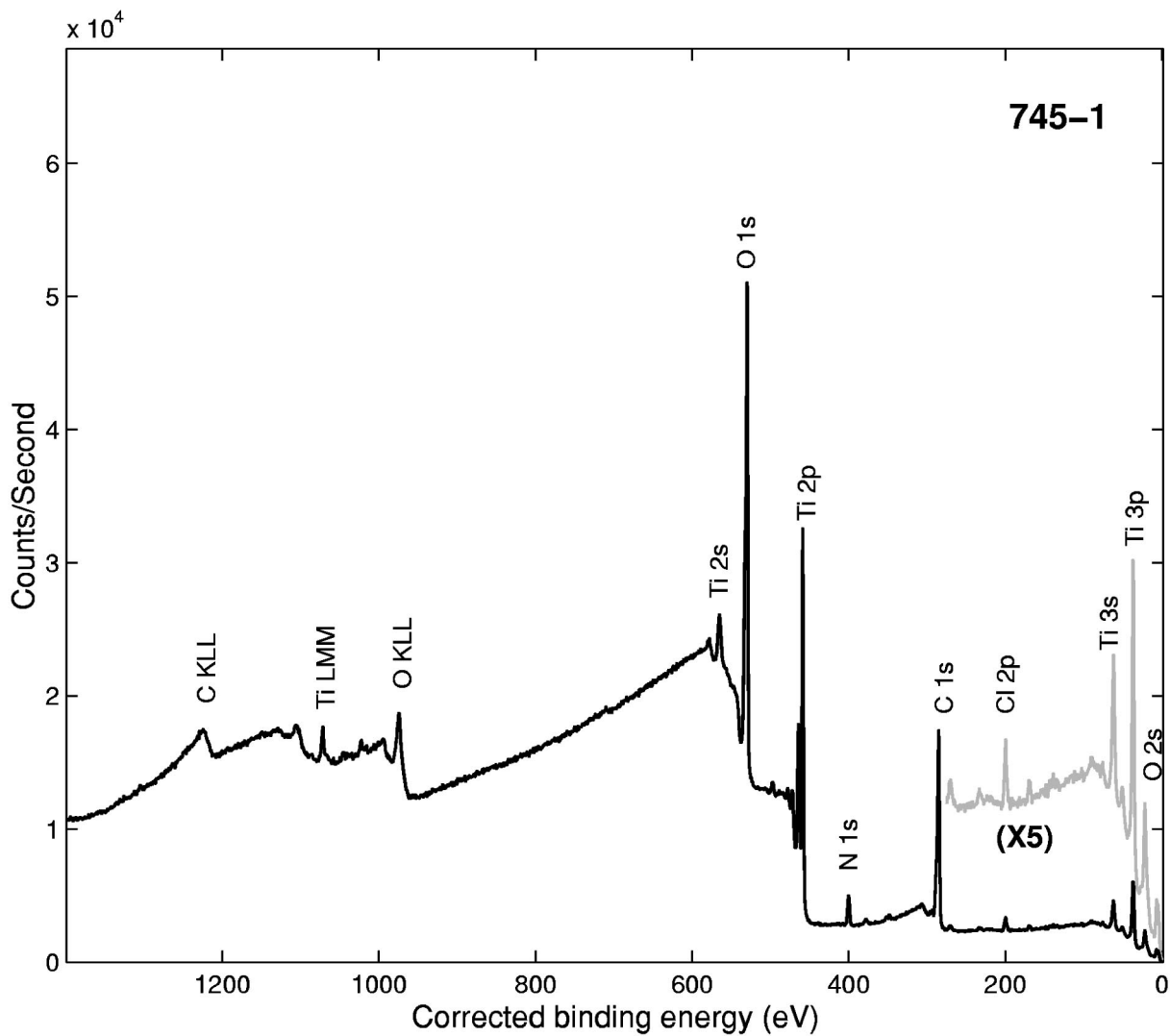
GUIDE TO FIGURES

Spectrum (Accession) #	Spectral Region	Voltage Shift*	Multiplier	Baseline	Comment #
745-1	Survey	+1.3	1	0	
745-2	O 1s	+1.3	1	0	
745-3	Ti 2p	+1.3	1	0	
745-4	C 1s	+1.3	1	0	
745-5	Ti 3s	+1.3	1	0	
745-6	Ti 3p	+1.3	1	0	
745-7	O 2s	+1.3	1	0	
745-8	Ti 3p	+0.97	1	0	
745-9	O 2s	+0.97	1	0	
745-10	Valence band	+0.97	1	0	
745-11 [NP]**	Au 4f	0	1	0	1
745-12 [NP]	Ag 3d	0	1	0	1
745-13 [NP]	Cu 2p	0	1	0	1

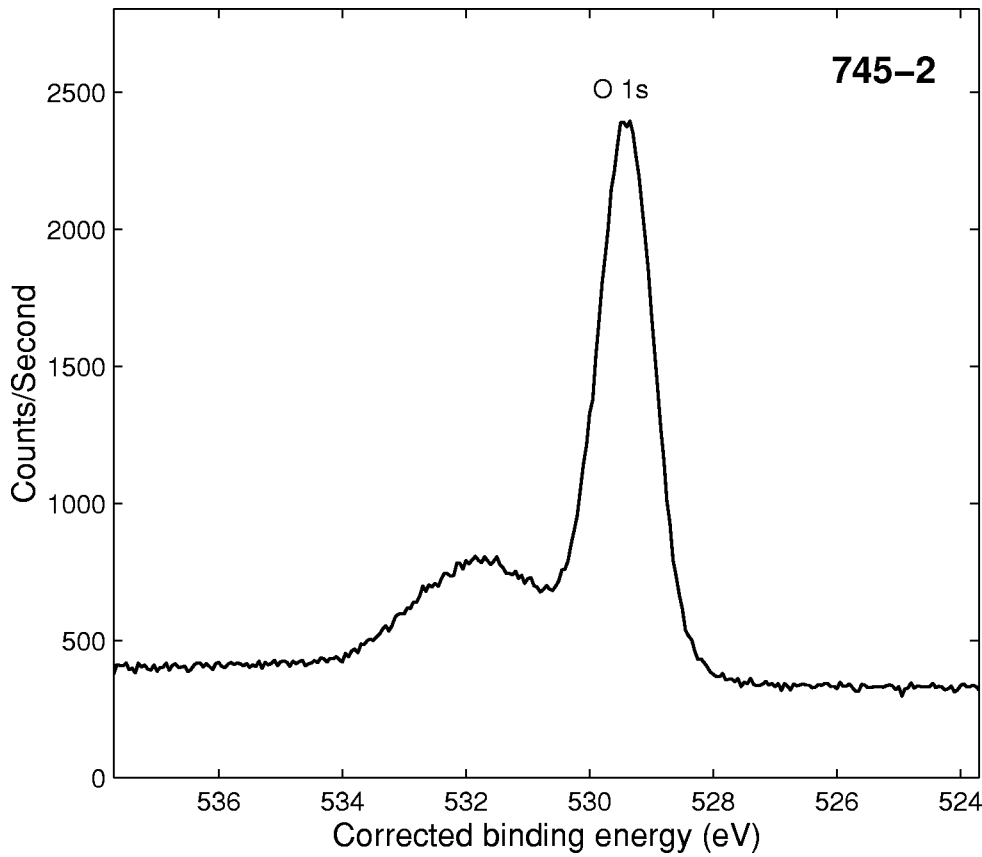
* Voltage shift of the archived (as-measured) spectrum relative to the printed figure. The figure reflects the recommended energy scale correction due to a calibration correction, sample charging, flood gun, or other phenomenon.

** [NP] signifies not published; digital spectra are archived in SSS database but not reproduced in the printed journal.

1. Calibration spectrum

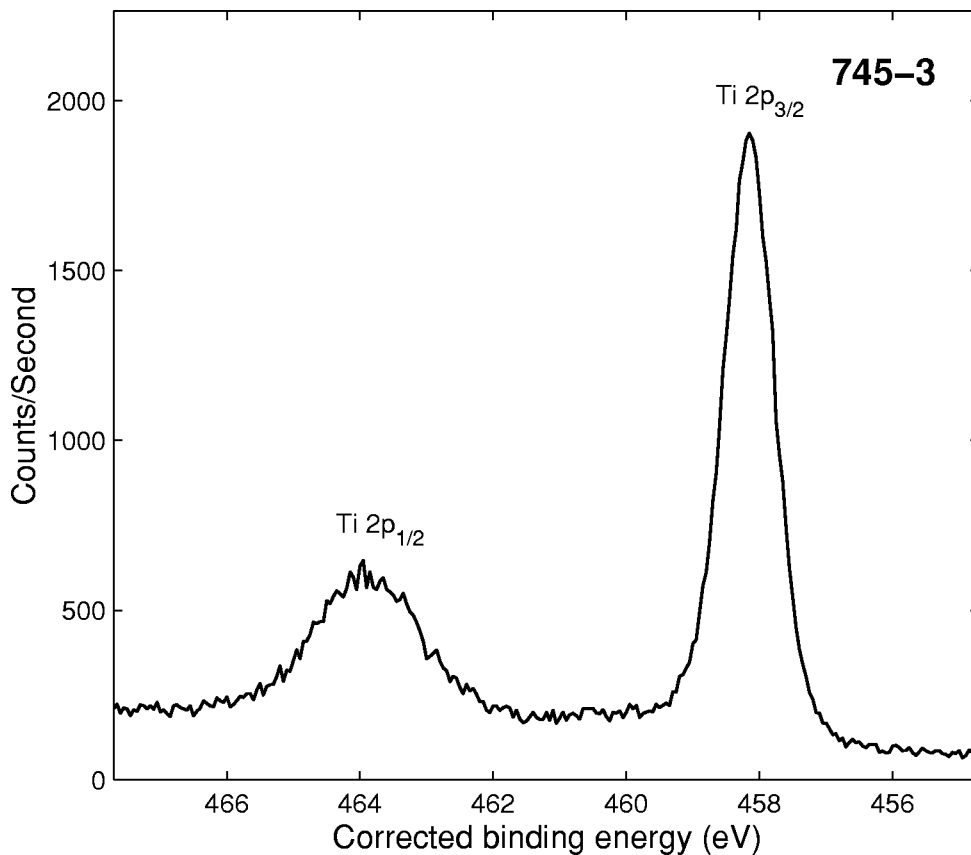


Accession #	00745-01
Host Material	TiO ₂ (001) anatase crystal
Technique	XPS
Spectral Region	survey
Instrument	Physical Electronics, Inc. 5500
Excitation Source	Al K _α monochromatic
Source Energy	1486.6 eV
Source Strength	225 W
Source Size	N/A
Analyzer Type	spherical sector
Incident Angle	45°
Emission Angle	45°
Analyzer Pass Energy	187.85 eV
Analyzer Resolution	1.879 eV
Total Signal Accumulation Time	2627 s
Total Elapsed Time	not specified
Number of Scans	15
Effective Detector Width	12.8 eV



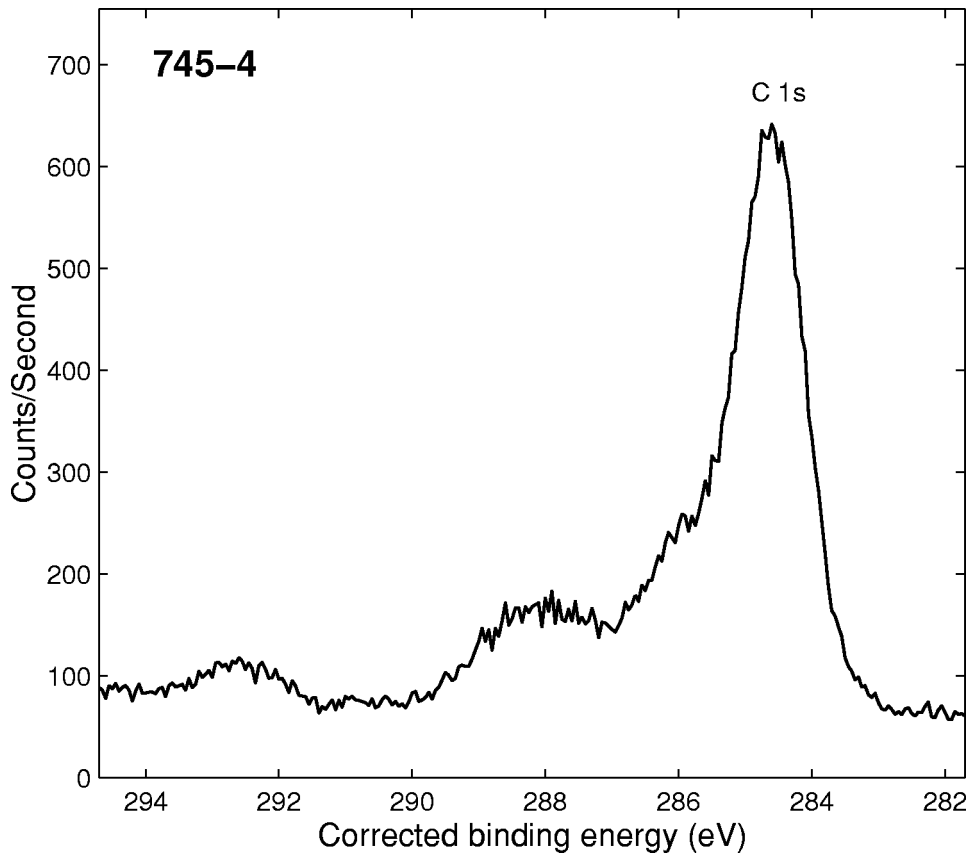
■ **Accession #:** 00745-02
 ■ **Host Material:** TiO₂ (001)
 anatase crystal
 ■ **Technique:** XPS
 ■ **Spectral Region:** O 1s

Instrument: Physical Electronics,
 Inc. 5500
 Excitation Source: Al K_α
 monochromatic
 Source Energy: 1486.6 eV
 Source Strength: 225 W
 Source Size: N/A
 Incident Angle: 45°
 Analyzer Type: spherical sector
 Analyzer Pass Energy: 5.850 eV
 Analyzer Resolution: 0.059 eV
 Emission Angle: 45°
 Total Signal Accumulation Time:
 1152 s
 Total Elapsed Time: not specified
 Number of Scans: 41
 Effective Detector Width: 0.8 eV



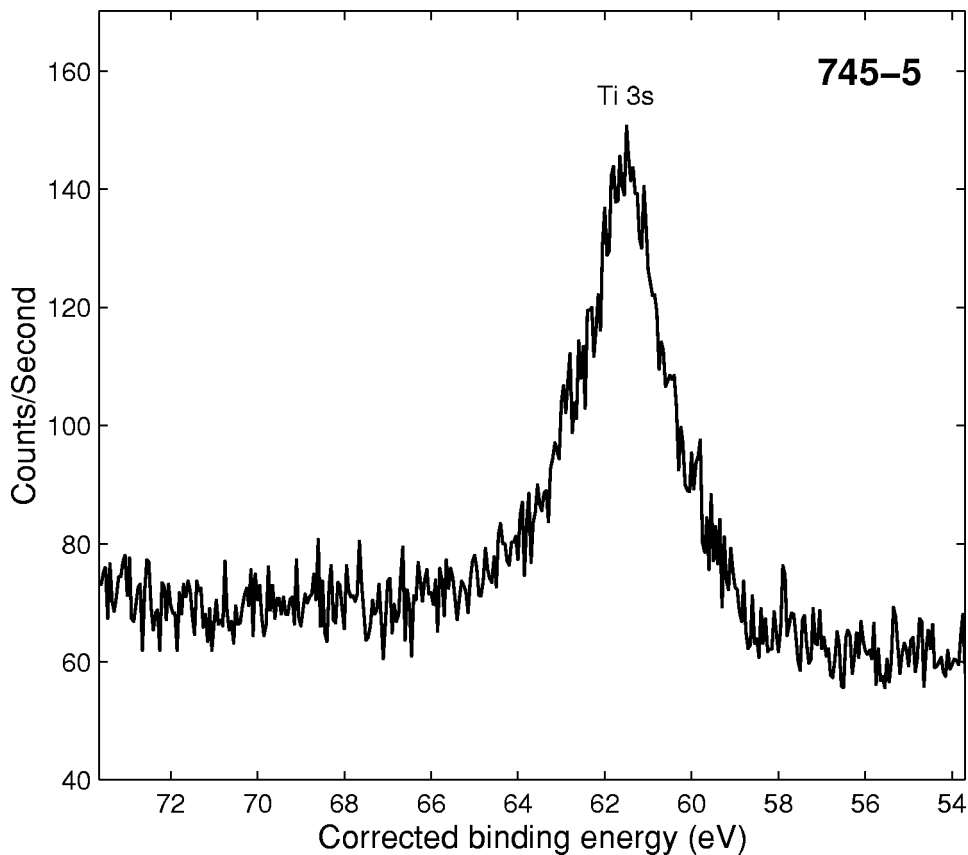
■ **Accession #:** 00745-03
 ■ **Host Material:** TiO₂ (001)
 anatase crystal
 ■ **Technique:** XPS
 ■ **Spectral Region:** Ti 2p

Instrument: Physical Electronics,
 Inc. 5500
 Excitation Source: Al K_α
 monochromatic
 Source Energy: 1486.6 eV
 Source Strength: 225 W
 Source Size: N/A
 Incident Angle: 45°
 Analyzer Type: spherical sector
 Analyzer Pass Energy: 5.850 eV
 Analyzer Resolution: 0.059 eV
 Emission Angle: 45°
 Total Signal Accumulation Time:
 365 s
 Total Elapsed Time: not specified
 Number of Scans: 14
 Effective Detector Width: 0.8 eV



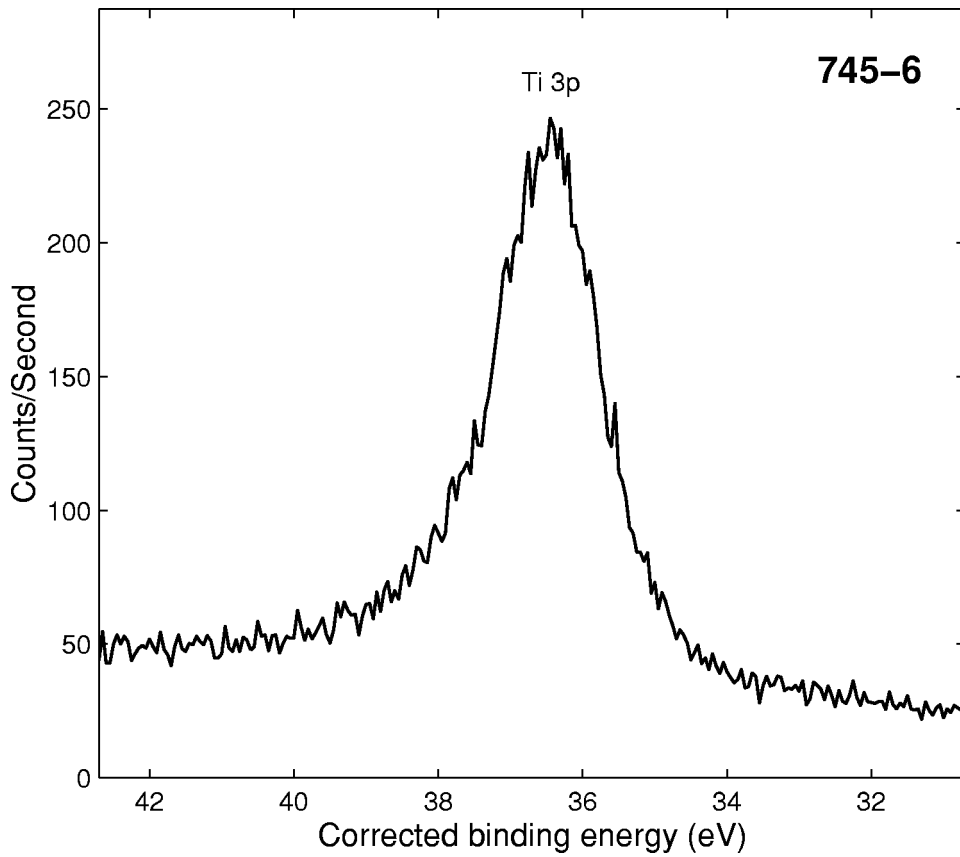
■ **Accession #:** 00745-04
 ■ **Host Material:** TiO₂ (001)
 anatase crystal
 ■ **Technique:** XPS
 ■ **Spectral Region:** C 1s

Instrument: Physical Electronics,
 Inc. 5500
 Excitation Source: Al K_α
 monochromatic
 Source Energy: 1486.6 eV
 Source Strength: 225 W
 Source Size: N/A
 Incident Angle: 45°
 Analyzer Type: spherical sector
 Analyzer Pass Energy: 5.850 eV
 Analyzer Resolution: 0.059 eV
 Emission Angle: 45°
 Total Signal Accumulation Time:
 835.2 s
 Total Elapsed Time: not specified
 Number of Scans: 32
 Effective Detector Width: 0.8 eV



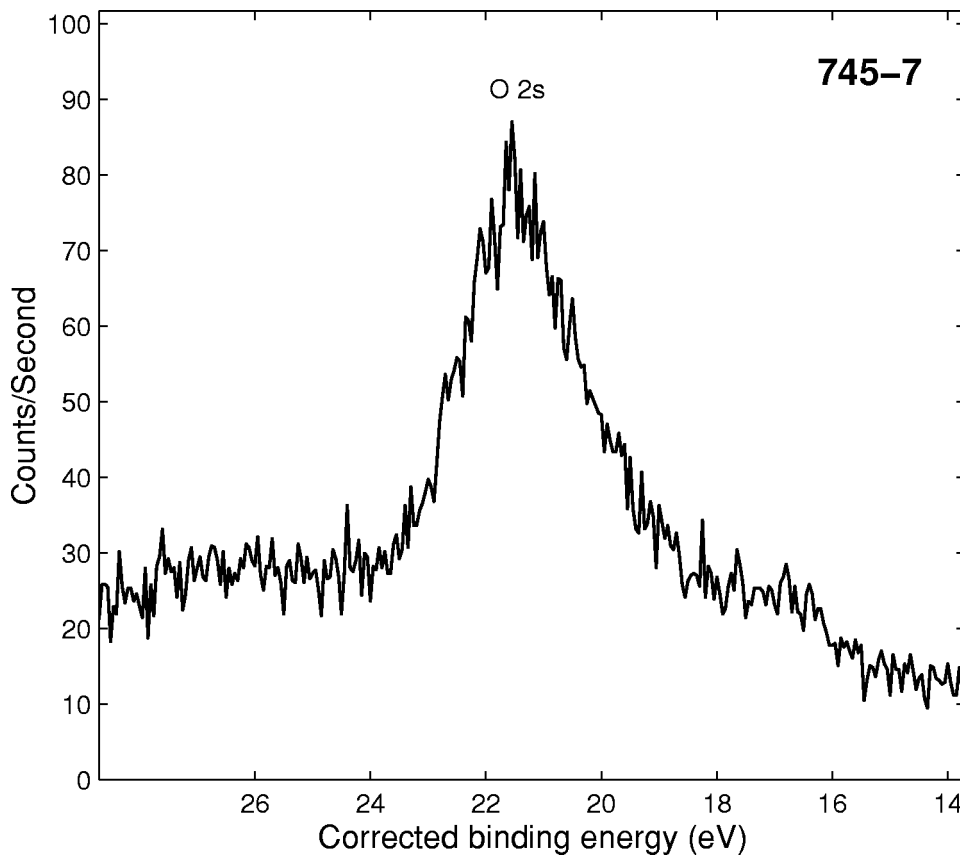
■ **Accession #:** 00745-05
 ■ **Host Material:** TiO₂ (001)
 anatase crystal
 ■ **Technique:** XPS
 ■ **Spectral Region:** Ti 3s

Instrument: Physical Electronics,
 Inc. 5500
 Excitation Source: Al K_α
 monochromatic
 Source Energy: 1486.6 eV
 Source Strength: 225 W
 Source Size: N/A
 Incident Angle: 45°
 Analyzer Type: spherical sector
 Analyzer Pass Energy: 5.850 eV
 Analyzer Resolution: 0.059 eV
 Emission Angle: 45°
 Total Signal Accumulation Time:
 1644 s
 Total Elapsed Time: not specified
 Number of Scans: 41
 Effective Detector Width: 0.8 eV



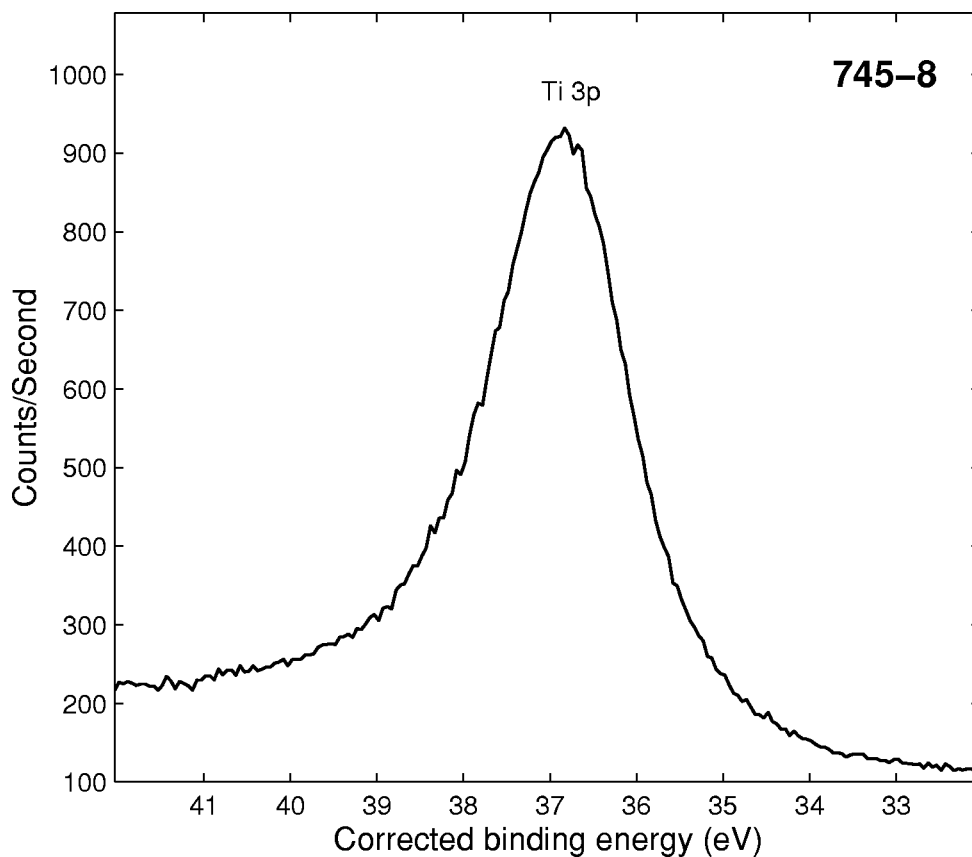
■ **Accession #:** 00745-06
 ■ **Host Material:** TiO₂ (001)
 anatase crystal
 ■ **Technique:** XPS
 ■ **Spectral Region:** Ti 3p

Instrument: Physical Electronics,
 Inc. 5500
 Excitation Source: Al K_α
 monochromatic
 Source Energy: 1486.6 eV
 Source Strength: 225 W
 Source Size: N/A
 Incident Angle: 45°
 Analyzer Type: spherical sector
 Analyzer Pass Energy: 5.850 eV
 Analyzer Resolution: 0.059 eV
 Emission Angle: 45°
 Total Signal Accumulation Time:
 988.2 s
 Total Elapsed Time: not specified
 Number of Scans: 41
 Effective Detector Width: 0.8 eV



■ **Accession #:** 00745-07
 ■ **Host Material:** TiO₂ (001)
 anatase crystal
 ■ **Technique:** XPS
 ■ **Spectral Region:** O 2s

Instrument: Physical Electronics,
 Inc. 5500
 Excitation Source: Al K_α
 monochromatic
 Source Energy: 1486.6 eV
 Source Strength: 225 W
 Source Size: N/A
 Incident Angle: 45°
 Analyzer Type: spherical sector
 Analyzer Pass Energy: 5.850 eV
 Analyzer Resolution: 0.059 eV
 Emission Angle: 45°
 Total Signal Accumulation Time:
 1234.2 s
 Total Elapsed Time: not specified
 Number of Scans: 41
 Effective Detector Width: 0.8 eV



■ **Accession #:** 00745-08
 ■ **Host Material:** TiO₂ (001)
 anatase crystal
 ■ **Technique:** XPS
 ■ **Spectral Region:** Ti 3p

Instrument: Physical Electronics,
 Inc. 5500

Excitation Source: Al K_α
 monochromatic

Source Energy: 1486.6 eV

Source Strength: 200 W

Incident Angle: 45°

Analyzer Type: spherical sector

Analyzer Pass Energy: 23.50 eV

Analyzer Resolution: 0.235 eV

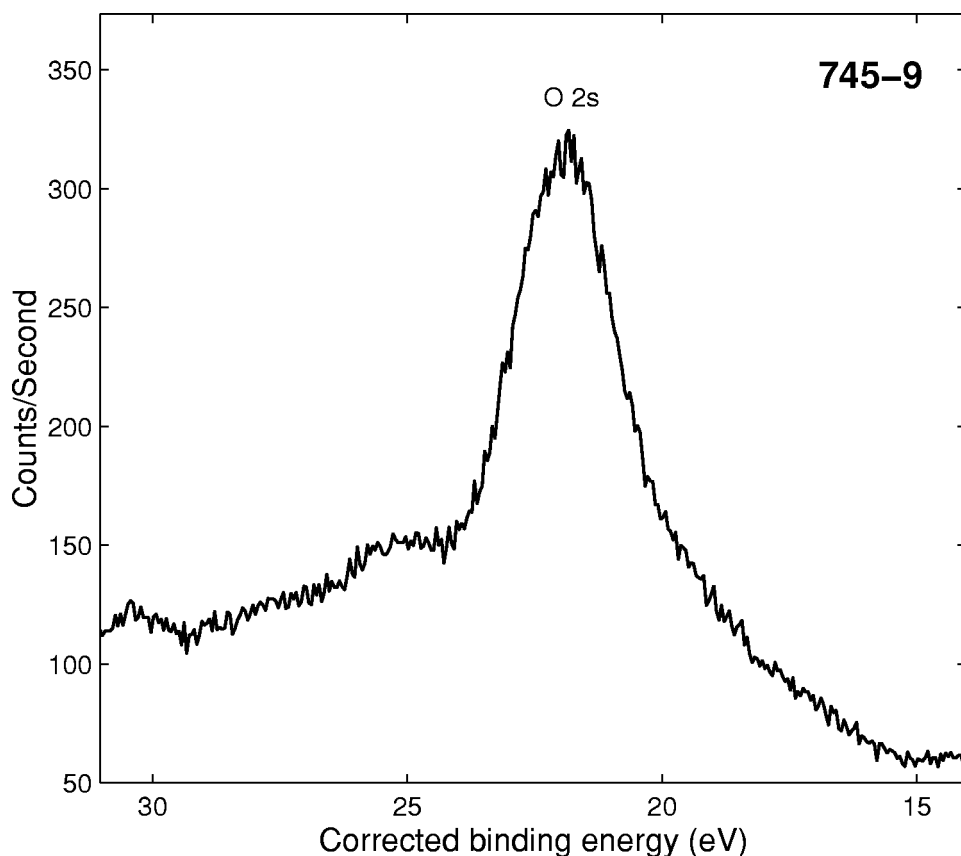
Emission Angle: 45°

Total Signal Accumulation Time:
 2412 s

Number of Scans: 120

Effective Detector Width: 0.8 eV

Comment: Ti 3p region with lower
 resolution and longer
 acquisition time.



■ **Accession #:** 00745-09
 ■ **Host Material:** TiO₂ (001)
 anatase crystal
 ■ **Technique:** XPS
 ■ **Spectral Region:** O 2s

Instrument: Physical Electronics,
 Inc. 5500

Excitation Source: Al K_α
 monochromatic

Source Energy: 1486.6 eV

Source Strength: 200 W

Incident Angle: 45°

Analyzer Type: spherical sector

Analyzer Pass Energy: 23.50 eV

Analyzer Resolution: 0.235 eV

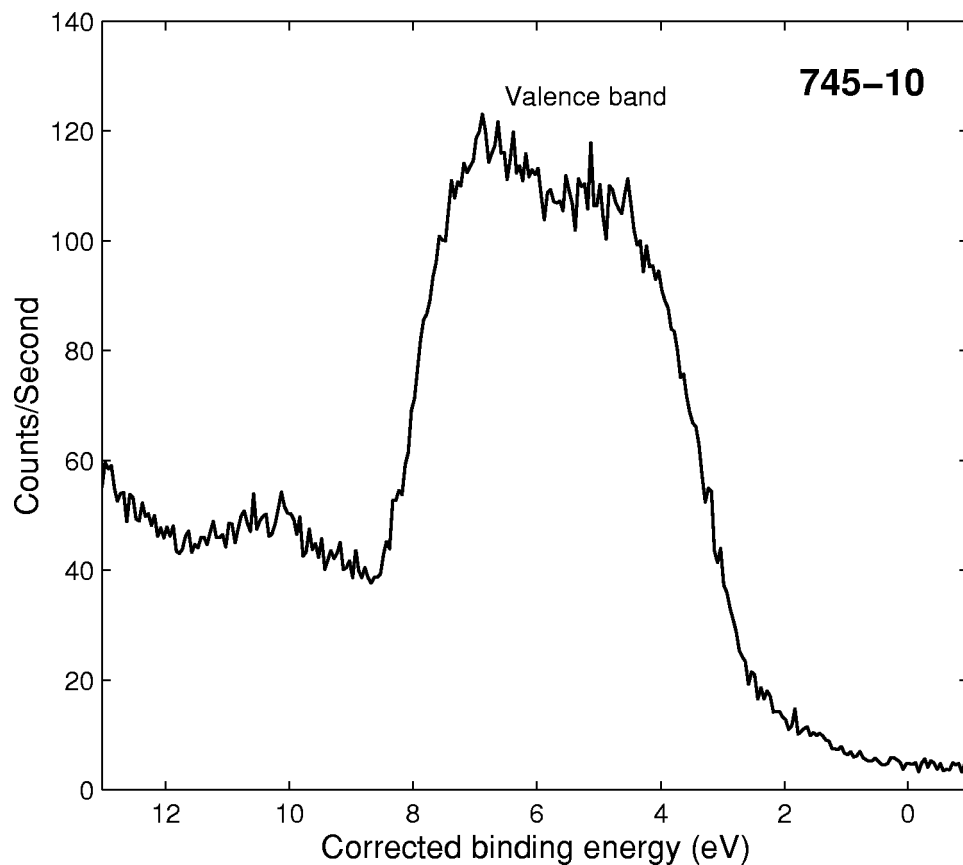
Emission Angle: 45°

Total Signal Accumulation Time:
 4092 s

Number of Scans: 120

Effective Detector Width: 0.8 eV

Comment: O 2s region with lower
 resolution and longer
 acquisition time.



-
- **Accession #:** 00745-10
 - **Host Material:** TiO₂ (001)
anatase crystal
 - **Technique:** XPS
 - **Spectral Region:** valence band

Instrument: Physical Electronics,
Inc. 5500

Excitation Source: Al K_α
monochromatic

Source Energy: 1486.6 eV

Source Strength: 200 W

Source Size: N/A

Incident Angle: 45°

Analyzer Type: spherical sector

Analyzer Pass Energy: 23.50 eV

Analyzer Resolution: 0.235 eV

Emission Angle: 45°

Total Signal Accumulation Time:
3372 s

Total Elapsed Time: not specified

Number of Scans: 120

Effective Detector Width: 0.8 eV

Comment: The two broad peaks
are the bonding and
non-bonding contributions of
the O 2p levels to the valence
band.
