Epitaxial CrN(001) Grown and Analyzed *In situ* by XPS and UPS. I. Analysis of As-deposited Layers

R. T. Haasch, T. -Y. Lee, D. Gall, J. E. Greene, and I. Petrov
Center for Microanalysis of Materials, Frederick Seitz Materials Research Laboratory, and the Materials Science Department, University of Illinois at Urbana-Champaign, Urbana, IL 61801

X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS) were used to characterize as-deposited epitaxial CrN(001) layers grown *in situ*. The films were deposited on MgO(001) at 650 °C in pure N_2 discharges maintained at a pressure of 5 mTorr (0.67 Pa). Mg K_α and monochromatic Al K_α sources were used to obtain the XPS spectra, while the UPS data was generated by He I and He II UV radiation. Analysis of the results show that the CrN(001) surfaces are free of O and C. A distinct splitting of the Cr $2p_{3/2}$ line is also observed. The films were found to be stoichiometric with Rutherford backscattering spectroscopy (RBS) results, yielding a N/Cr ratio of 1.04±0.02. However, composition determined by XPS (N/Cr=0.73) show an excess of chromium.

Accession # 00623
Technique: XPS, UPS
Host Material: epitaxial CrN(001) thin film as-deposited
Instrument: Physical Electronics, Inc. 5400
Major Elements in Spectrum: Cr, N
Minor Elements in Spectrum: none
Printed Spectra: 8
Spectra in Electronic Record: 12
Spectral Category: comparison
Original Submission: 12/21/2000
Accepted for Publication: 1/23/2001

Keywords: *chromium nitride; magnetron sputtering; hard coatings; transition metal nitrides*

PACS: *81.05.Je, 82.80.Pv, 79.60.Dp, 81.15.Cd*

SPECIMEN DESCRIPTION

Host Material: epitaxial CrN(001) thin film as-deposited

CAS Registry #: 24094-93-7

Host Material Characteristics: homogeneous; solid; single crystal; conductor; inorganic compound; thin film

Chemical Name: chromium nitride

Source: epitaxially grown *in situ* on MgO(001) by reactive magnetron sputtering

Host Composition: CrN

Form: epitaxial thin film

Structure: B1-NaCl structure

History & Significance: In order to identify the stoichiometry of transition metal nitrides, reference spectra from samples of known composition are needed. Stoichiometric single-crystal transition metal nitride films were grown in an UHV magnetron sputter deposition system attached to a photoelectron spectrometer. Spectra were obtained from as-deposited films without exposure to air. The as-deposited bulk film composition was verified using RBS.

As Received Condition: direct vacuum transfer from growth chamber

Analyzed Region: same as host material

***Ex Situ* Preparation/Mounting:** The MgO substrate was mechanically mounted using Mo clips spot-welded to a Mo substrate heater.

***In Situ* Preparation:** The epitaxial CrN(001) layers were grown in a multichamber UHV system. The turbomolecular-pumped growth chamber, having a base pressure of 3×10^{-9} Torr (4×10^{-7} Pa), was equipped with a dc magnetron and was isolated from the analytical chamber of the instrument during growth. MgO(001) substrates ($5 \times 5 \times 0.5$ mm) were annealed at T_s = 850 °C for 2 h prior to deposition, a procedure that has been shown (Ref. 1) to produce sharp 1×1 RHEED patterns. The target, a 5-cm-diam water-cooled Cr disk (99.97%), was cleaned with a N_2 discharge prior to film growth. Depositions were carried out at T_s = 650 °C in pure N_2 (99.9999%) at a total pressure of 5 mTorr (0.67 Pa) with the substrate grounded. The discharge current and voltage were 0.4 A and 500 V, respectively, while the target-to-substrate separation was 6.5 cm resulting in a film deposition rate of 36 nm/min. The total film thickness was 250 nm. The composition of the films was determined by RBS using 2 MeV He^+ at a scattering angle of 150°. Quantitative analysis was done using the surface height method (Ref. 2) yielding a N/Cr ratio of 1.04 ± 0.02.

Pre-Analysis Beam Exposure: approximately 10 s for the XPS spectra and 1 min for the UPS spectra; no x-ray or ultraviolet effects observed

Charge Control: No charge control was used. No surface charging was observed.

Temp. During Analysis: 300 K

Pressure During Analysis: $<3.0\times10^{-7}$ Pa

INSTRUMENT DESCRIPTION

Manufacturer and Model: Physical Electronics, Inc. 5400

Analyzer Type: spherical sector

Detector: position sensitive detector

Number of Detector Elements: 64

Deviations from Standard Analyzer or Lens: Physical Electronics Analyzer Model 10-360, Omni-Focus lens (small area).

INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA

■ *Spectrometer*

Analyzer Mode: constant pass energy

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

Throughput Comment: The energy-independent instrument throughput function results from the $1/E$ throughput of the spherical analyzer and the E dependence of the input lens throughput. The angular acceptance angle θ, as provided by the

vendor, is given in terms of the magnification M (M=1 for large area and 3 for small area lens modes); the pass energy PE; and the photoelectron kinetic energy KE by $\theta = 7.5M \times \sqrt{\text{PE/KE}}$.

Excitation Source Window: 2 μm aluminum window on Mg K_α

Signal Mode: multichannel direct

Comment: He I source: The ultraviolet lamp was tuned to a consistent apricot color of the visible portion of the discharge. A pressure gauge was not available on the gas inlet of the lamp. The nominal conditions of the discharge were: 520 V, 55 mA, and a chamber pressure of 9×10^{-6} Pa. He II source: The ultraviolet lamp was tuned to a consistent blue-white color of the visible portion of the discharge. A pressure gauge was not available on the gas inlet of the lamp. The nominal conditions of the discharge were: 580 V, 56 mA, and a chamber pressure of 4×10^{-6} Pa.

■ *Geometry*

Incident Angle: varies by spectrum

Source to Analyzer Angle: varies by spectrum

Emission Angle: varies by spectrum

Specimen Azimuthal Angle: 0°

Acceptance Angle from Analyzer Axis: 0°

Comments: Incident angles: Monochromated Al K_α, 45°; Mg K_α, 9.7°; He, 50°. Source-to-analyzer angles: Monchromated Al K_α, 90°; Mg K_α, 54.7°; He, 60°. Emission angles: Monochromated Al K_α and Mg K_α, 45°; He, 90°.

DATA ANALYSIS METHOD

Energy Scale Correction: XPS binding energy scales for spectra collected with monochromated Al K_α were corrected using Au $4f_{7/2}$=84.0 and Cu $2p_{3/2}$=932.7. All other data did not require energy scale correction.

Recommended Energy-Scale Shift: Accession #s 623-01, -02 and -03, 0.2 eV is added to the original scale.

Peak Shape and Background Method: A Shirley function was used for background corrections. Asymmetric Gaussian–Lorentzian line shapes were used to fit the Cr 2*p* and N 1*s* regions. (Software provided by Physical Electronics, Inc.)

Quantitation Method: Spectra were peak fitted to determine area. Peak areas were corrected, by dividing by the applicable relative sensitivity factor, and summed. Each corrected peak area was taken as a percentage of the total corrected peak area. (Software provided by Physical Electronics, Inc.)

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of the Department of Energy, under Contract No. DEFG02-96-ER45439 and the use of the facilities of the Center for Microanalysis of Materials, which is partially supported by DOE, at the University of Illinois.

REFERENCES

1. R. C. Powell, G. A. Tomasch, Y. W. Kim, J. A. Thornton, and J. E. Greene, in *Diamond, Silicon Carbide and Related Wide Bandgap Semiconductors*, edited by J. R. Glass, R. F. Messier, and N. Fujimori (MRS, Pittsburgh, 1990), p. 525.
2. W. K. Chu, J. W. Mayer, and M. A. Nicolet, *Backscattering Spectrometry* (Academic, New York, 1978), p. 81.

SPECTRAL FEATURES TABLE

Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV-cts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
00623-02[a]	Cr $2p_{3/2}$	574.3	0.99	681	2.201	57.7	CrN
00623-02[a]	Cr $2p_{3/2}$	575.4	1.15	1659	⋯	⋯	CrN
00623-02[b]	⋯	580.1	8.00	750	⋯	⋯	⋯
00623-02	Cr $2p_{1/2}$	583.9	1.23	340	⋯	⋯	CrN
00623-02	Cr $2p_{1/2}$	585.0	1.28	829	⋯	⋯	CrN
00623-03	N 1*s*	396.7	0.87	676	0.477	42.3	CrN
00623-05[a]	Cr $2p_{3/2}$	574.4	1.36	4774	2.427	57.7	CrN
00623-05[a]	Cr $2p_{3/2}$	575.4	1.44	8795	⋯	⋯	CrN
00623-05[b]	⋯	576.9	1.55	2387	⋯	⋯	⋯
00623-05[b]	⋯	579.0	6.00	5216	⋯	⋯	⋯
00623-05	Cr $2p_{1/2}$	584.0	1.66	2387	⋯	⋯	CrN
00623-05	Cr $2p_{1/2}$	585.1	1.60	4397	⋯	⋯	CrN
00623-05[b]	⋯	586.5	1.55	1193	⋯	⋯	⋯
00623-06	N 1*s*	396.7	1.06	4199	0.477	42.3	CrN

[a] This feature was assigned to account for the evidence of structure most likely due to a final-state relaxation.
[b] This feature was added to aid in the curve-fitting process.

Comment to Spectral Features Table: Due to the splitting of the $2p_{3/2}$ line and a possible overlap with a plasmon-loss peak, several features were used in the process of fitting the Cr 2*p* region. The $2p_{3/2}$–$2p_{1/2}$ separation was fixed at 9.6 eV.

Footnote to Spectrum 00623-07: The valence band photoelectron spectrum was obtained at an electron emission angle of 90° (relative to the sample surface); thus the emitted photoelectrons had a crystal momentum along the <001> direction. However, due to the finite acceptance angle of the analyzer extraction lenses, 22°, the momentum of the measured electrons cannot be uniquely determined. Therefore, a relatively large fraction of *k*-space contributes to the spectrum. As a result, the He I spectrum consists of a sum of broad features from the total density-of-states (DOS).

Footnote to Spectrum 00623-08: The valence band photoelectron spectrum was obtained at an electron emission angle of 90° (relative to the sample surface); thus the emitted photoelectrons had a crystal momentum along the <001> direction. However, due to the finite acceptance angle of the detector, 14°, the momentum of the measured electrons cannot be uniquely determined. Therefore, a relative large fraction of *k*-space contributes to the spectrum. As a result, the He II spectrum closely resembles the total density-of-states (DOS).

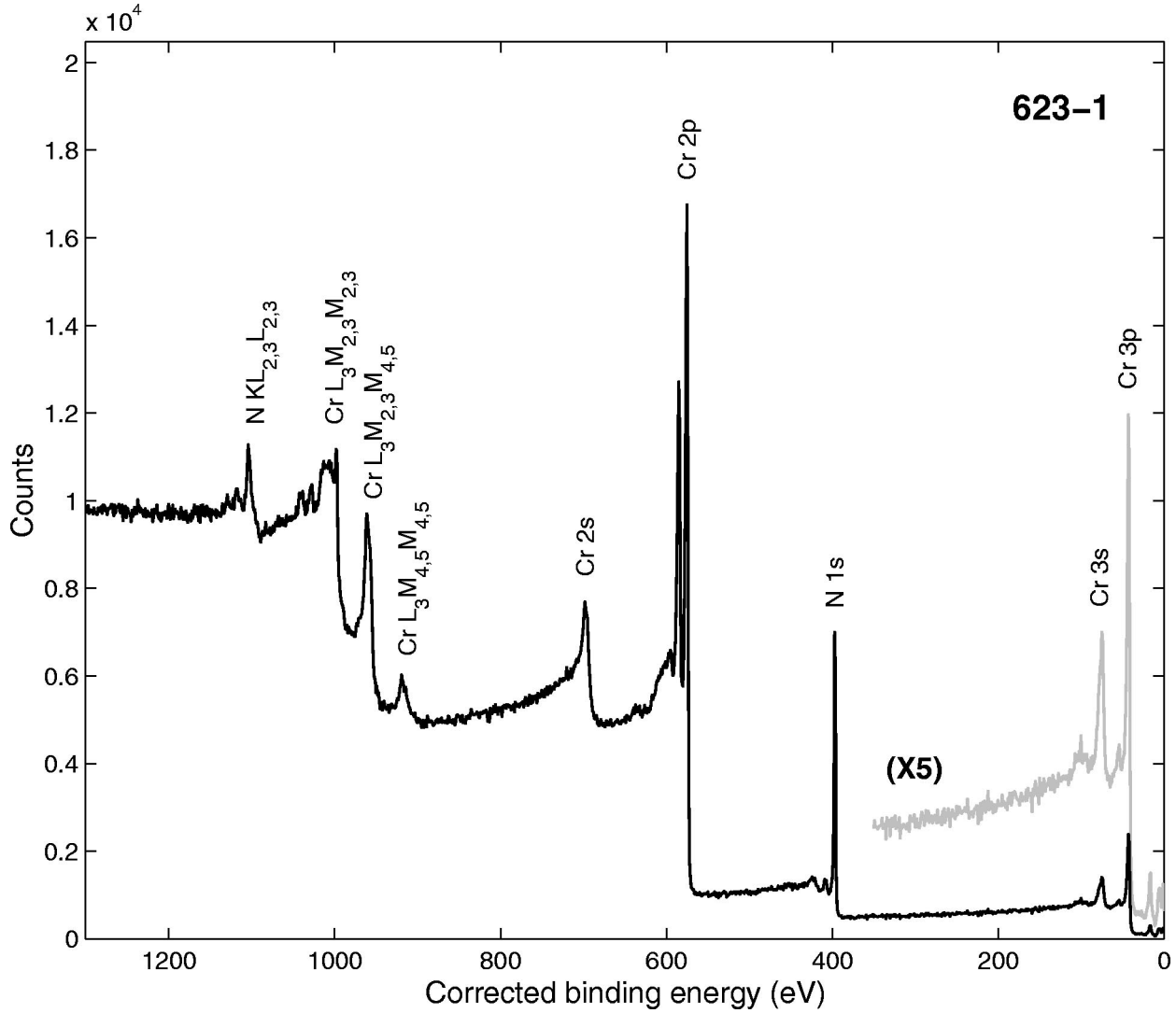
ANALYZER CALIBRATION TABLE

Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV-cts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
9	Au $4f_{7/2}$	83.8	0.86	6451	⋯	⋯	⋯
10	Cu $2p_{3/2}$	932.5	0.99	6952	⋯	⋯	⋯
11	Au $4f_{7/2}$	84.0	1.03	34261	⋯	⋯	⋯
12	Cu $2p_{3/2}$	932.7	1.19	59588	⋯	⋯	⋯

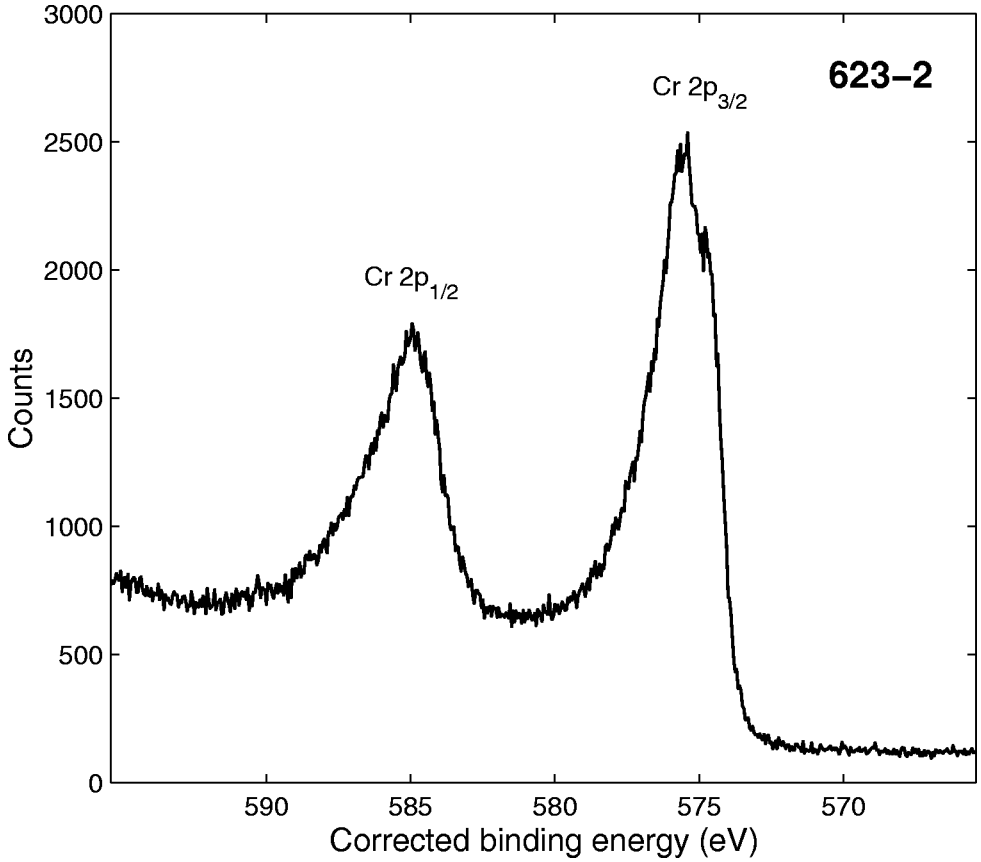
GUIDE TO FIGURES

Spectrum (Accession) #	Spectral Region	Sample Voltage*	Multiplier	Baseline	Comment #
623-1	Survey	−0.2	1	0	1
623-2	Cr $2p$	−0.2	1	0	1
623-3	N $1s$	−0.2	1	0	1
623-4	Survey	0	1	0	2
623-5	Cr $2p$	0	1	0	2
623-6	N $1s$	0	1	0	2
623-7	Valence band	0	1	0	3
623-8	Valence band	0	1	0	4
623-9 [NP]**	Au $4f$	−0.2	1	0	1, 5
623-10 [NP]	Cu $2p_{3/2}$	−0.2	1	0	1, 5
623-11 [NP]	Au $4f$	0	1	0	2, 5
623-12 [NP]	Cu $2p_{3/2}$	0	1	0	2, 5

*Inferred sample potential relative to spectrometer ground due to charging, flood gun, or other phenomena.
**[NP] signifies not published; digital spectra are archived in *SSS* database but not reproduced in the printed journal.
1. Monchromated Al K_α (1486.6 eV) excitation source
2. Mg K_α (1253.6 eV) excitation source
3. He I (21.2 eV) excitation source
4. He II (40.8 eV) excitation source
5. Calibration spectrum



Accession #	00623-01
Host Material	epitaxial CrN(001) thin film as-deposited
Technique	XPS
Spectral Region	survey
Instrument	Physical Electronics, Inc. 5400
Excitation Source	Al K_α monochromatic
Source Energy	1486.6 eV
Source Strength	500 W
Source Size	2000 μm × 2000 μm
Analyzer Type	spherical sector
Incident Angle	45°
Emission Angle	45°
Analyzer Pass Energy	178.95 eV
Analyzer Resolution	2.7 eV
Total Signal Accumulation Time	911 s
Total Elapsed Time	949 s
Number of Scans	7
Source Beam Size at Specimen Surface	2828 μm × 2000 μm
Effective Detector Width	2.7 eV
Analyzer Width	1414 μm × 1000 μm
Analyzer Angular Acceptance Width	22° × 22° at 190 eV



- **Accession #:** 00623-02
- **Host Material:** epitaxial CrN(001) thin film as-deposited
- **Technique:** XPS
- **Spectral Region:** Cr 2*p*

Instrument: Physical Electronics, Inc. 5400

Excitation Source: Al K_α monochromatic

Source Energy: 1486.6 eV

Source Strength: 500 W

Source Size: 2000 μm × 2000 μm

Incident Angle: 45°

Analyzer Type: spherical sector

Analyzer Pass Energy: 17.90 eV

Analyzer Resolution: 0.27 eV

Emission Angle: 45°

Total Signal Accumulation Time: 1683 s

Total Elapsed Time: 1805 s

Number of Scans: 28

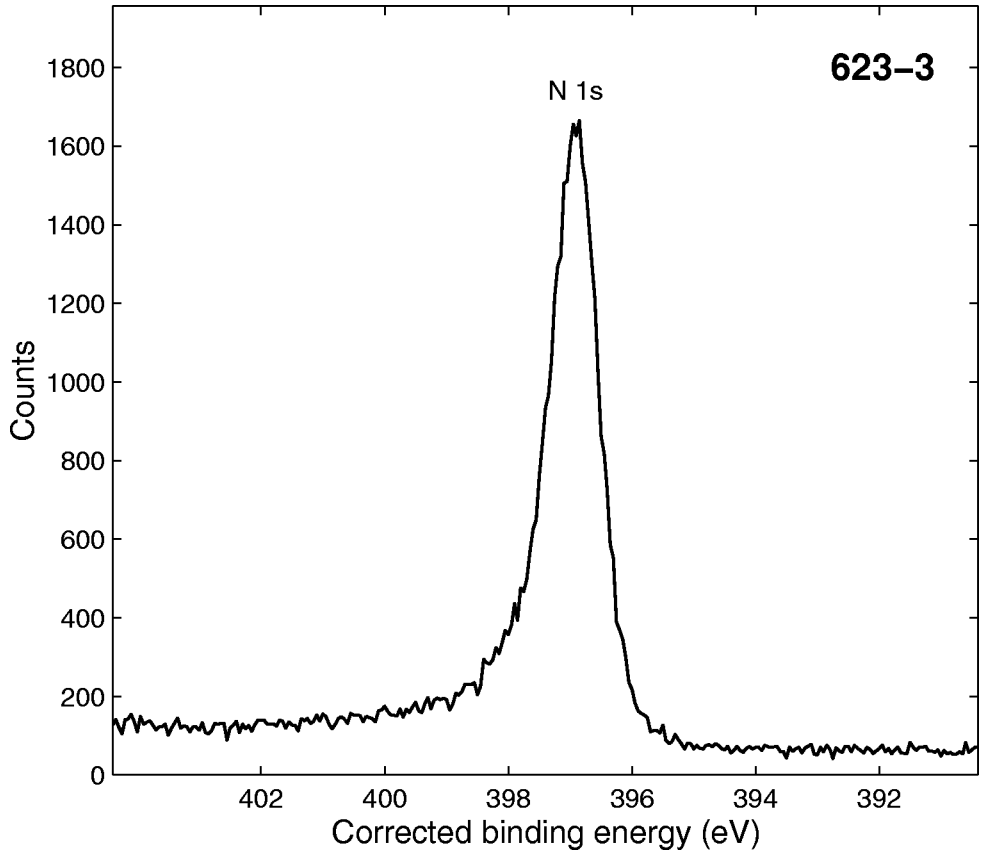
Source Beam Size at Specimen Surface: 2828 μm × 2000 μm

Effective Detector Width: 0.27 eV

Analyzer Width: 1414 μm × 1000 μm

Analyzer Angular Acceptance Width: 3° × 3° at 955 eV

Comment: The Cr 2$p_{3/2}$ line shows evidence of structure most likely due to a final-state relaxation.



- **Accession #:** 00623-03
- **Host Material:** epitaxial CrN(001) thin film as-deposited
- **Technique:** XPS
- **Spectral Region:** N 1*s*

Instrument: Physical Electronics, Inc. 5400

Excitation Source: Al K_α monochromatic

Source Energy: 1486.6 eV

Source Strength: 500 W

Source Size: 2000 μm × 2000 μm

Incident Angle: 45°

Analyzer Type: spherical sector

Analyzer Pass Energy: 17.90 eV

Analyzer Resolution: 0.27 eV

Emission Angle: 45°

Total Signal Accumulation Time: 787 s

Total Elapsed Time: 909 s

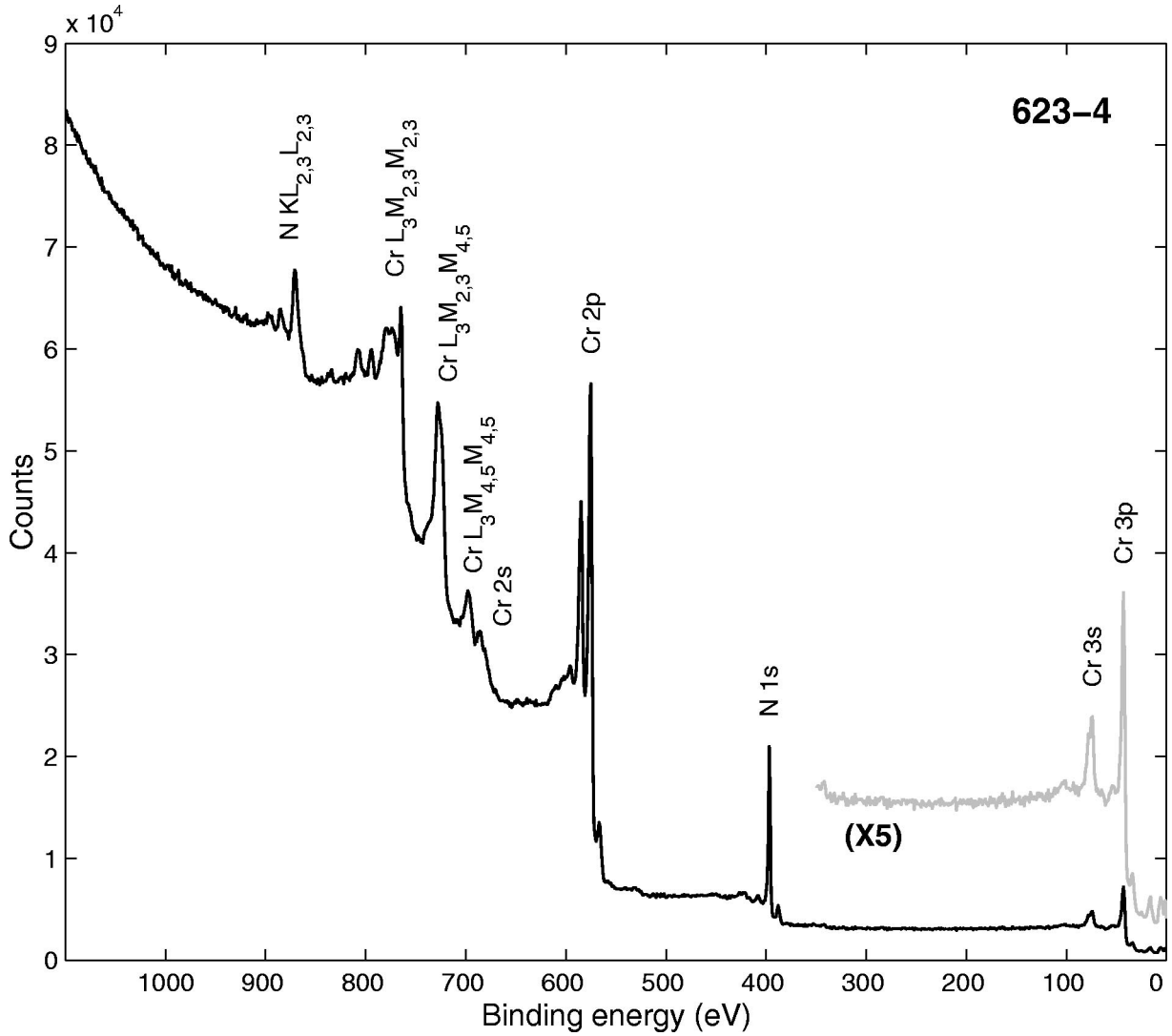
Number of Scans: 28

Source Beam Size at Specimen Surface: 2828 μm × 2000 μm

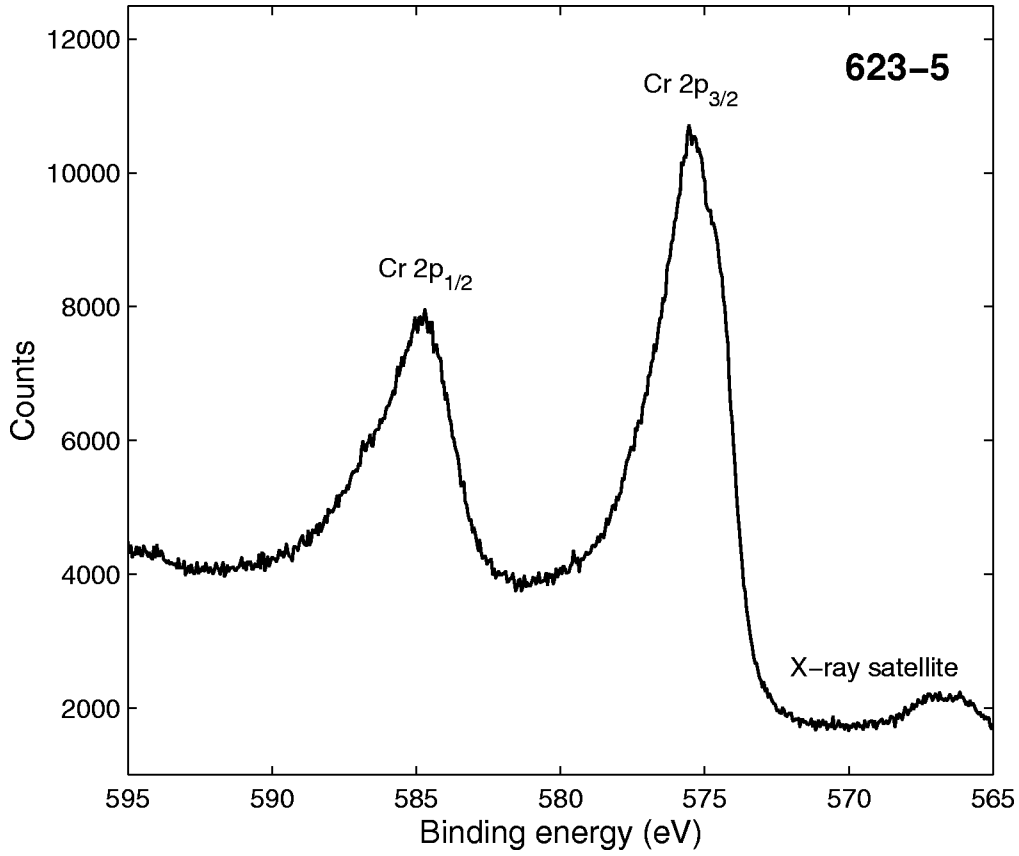
Effective Detector Width: 0.27 eV

Analyzer Width: 1414 μm × 1000 μm

Analyzer Angular Acceptance Width: 3° × 3° at 955 eV



Accession #	00623-04
Host Material	epitaxial CrN(001) thin film as-deposited
Technique	XPS
Spectral Region	survey
Instrument	Physical Electronics, Inc. 5400
Excitation Source	Mg K_α
Source Energy	1253.6 eV
Source Strength	400 W
Source Size	$>$25000 μm $\times$ $>$25000 μm
Analyzer Type	spherical sector
Incident Angle	9.7°
Emission Angle	45°
Analyzer Pass Energy	178.95 eV
Analyzer Resolution	2.7 eV
Total Signal Accumulation Time	330 s
Total Elapsed Time	352 s
Number of Scans	3
Source Beam Size at Specimen Surface	$>$25000 μm $\times$ $>$25000 μm
Effective Detector Width	2.7 eV
Analyzer Width	1414 μm $\times$ 1000 μm
Analyzer Angular Acceptance Width	24° $\times$ 24° at 150 eV



- **Accession #:** 00623-05
- **Host Material:** epitaxial CrN(001) thin film as-deposited
- **Technique:** XPS
- **Spectral Region:** Cr 2*p*

Instrument: Physical Electronics, Inc. 5400

Excitation Source: Mg K_α

Source Energy: 1253.6 eV

Source Strength: 400 W

Source Size: >25000 μm × >25000 μm

Incident Angle: 9.7°

Analyzer Type: spherical sector

Analyzer Pass Energy: 17.90 eV

Analyzer Resolution: 0.27 eV

Emission Angle: 45°

Total Signal Accumulation Time: 962 s

Total Elapsed Time: 1036 s

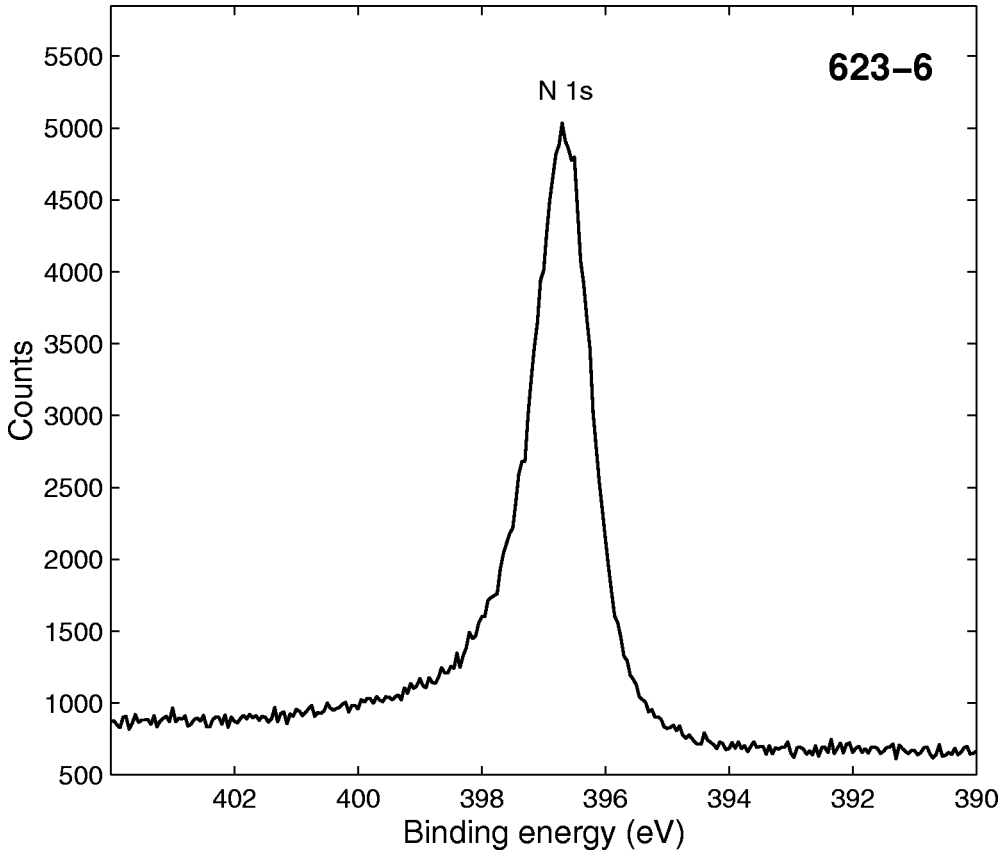
Number of Scans: 16

Source Beam Size at Specimen Surface: >25000 μm × >25000 μm

Effective Detector Width: 0.27 eV

Analyzer Width: 1414 μm × 1000 μm

Analyzer Angular Acceptance Width: 3° × 3° at 722 eV



- **Accession #:** 00623-06
- **Host Material:** epitaxial CrN(001) thin film as-deposited
- **Technique:** XPS
- **Spectral Region:** N 1*s*

Instrument: Physical Electronics, Inc. 5400

Excitation Source: Mg K_α

Source Energy: 1253.6 eV

Source Strength: 400 W

Source Size: >25000 μm × >25000 μm

Incident Angle: 9.7°

Analyzer Type: spherical sector

Analyzer Pass Energy: 17.90 eV

Analyzer Resolution: 0.27 eV

Emission Angle: 45°

Total Signal Accumulation Time: 449 s

Total Elapsed Time: 523 s

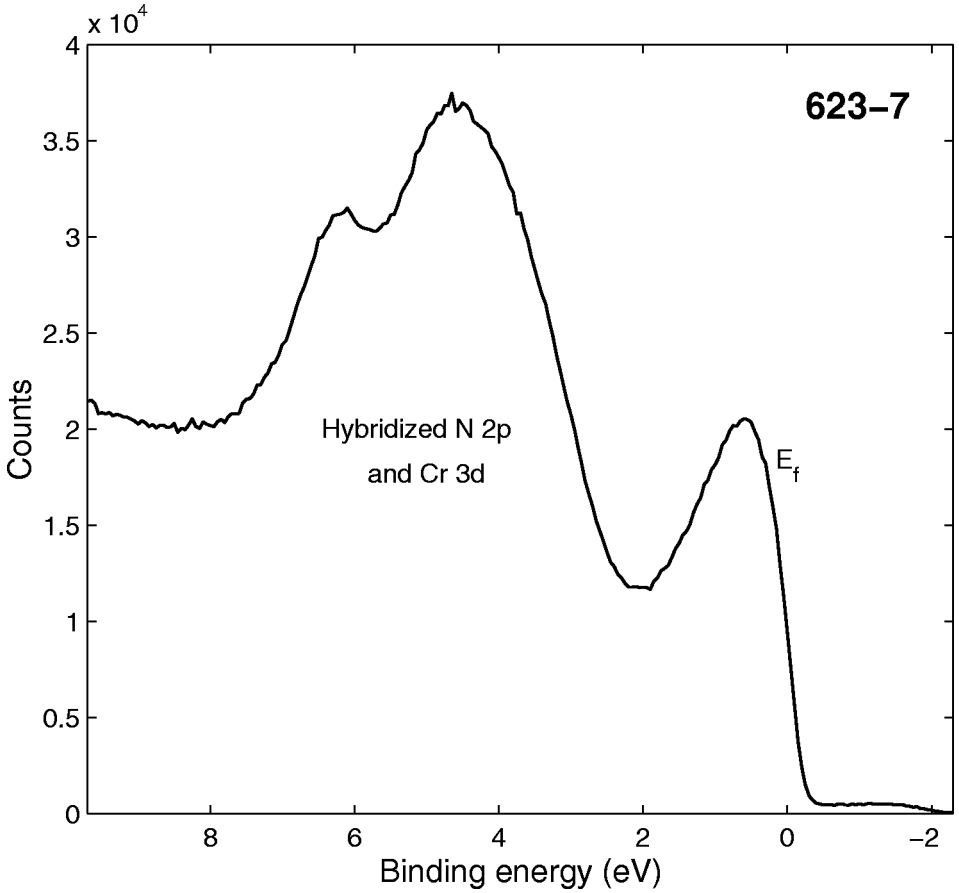
Number of Scans: 16

Source Beam Size at Specimen Surface: >25000 μm × >25000 μm

Effective Detector Width: 0.27 eV

Analyzer Width: 1414 μm × 1000 μm

Analyzer Angular Acceptance Width: 3° × 3° at 722 eV



- **Accession #:** 00623-07
- **Host Material:** epitaxial CrN(001) thin film as-deposited
- **Technique:** UPS
- **Spectral Region:** valence band

Instrument: Physical Electronics, Inc. 5400

Excitation Source: He I

Source Energy: 21.2 eV

Source Strength: 30 W

Source Size: >5000 μm × >5000 μm

Incident Angle: 50°

Analyzer Type: spherical sector

Analyzer Pass Energy: 8.95 eV

Analyzer Resolution: 0.13 eV

Emission Angle: 90°

Total Signal Accumulation Time: 120 s

Total Elapsed Time: 142 s

Number of Scans: 3

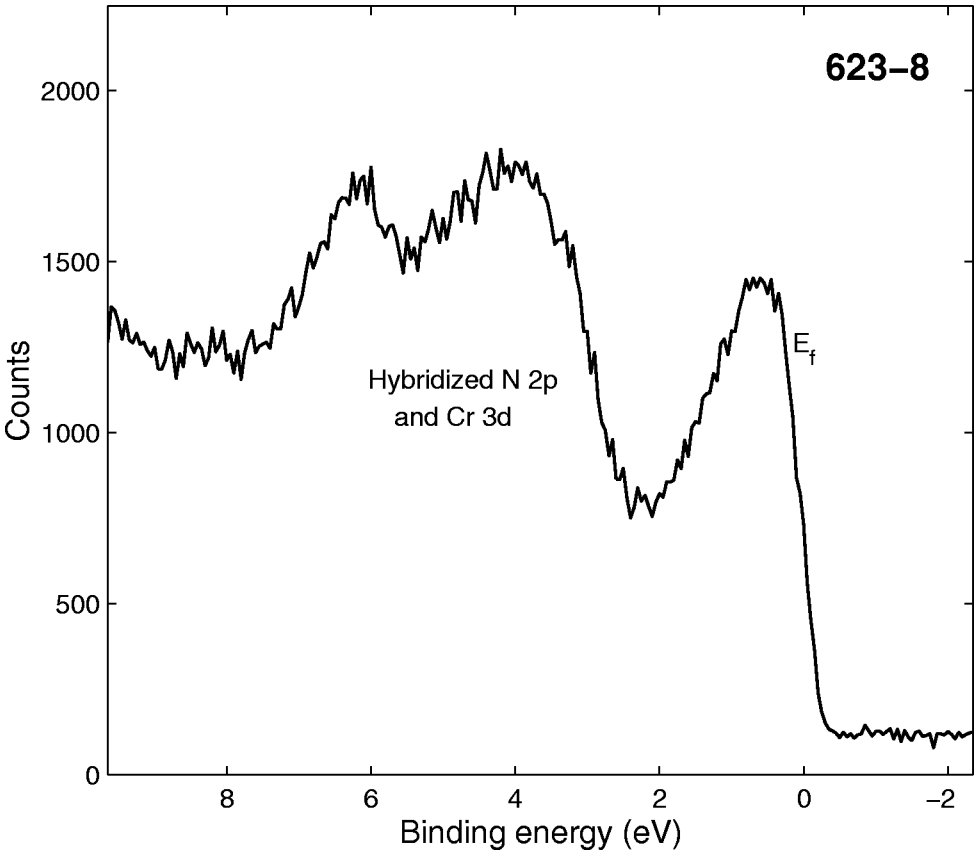
Source Beam Size at Specimen Surface: >5000 μm × >5000 μm

Effective Detector Width: 0.13 eV

Analyzer Width: 1000 μm × 1000 μm

Analyzer Angular Acceptance Width: 22° × 22° at 9 eV

Comment: See footnote below the Spectral Features Table.



- **Accession #:** 00623-08
- **Host Material:** epitaxial CrN(001) thin film as-deposited
- **Technique:** UPS
- **Spectral Region:** valence band

Instrument: Physical Electronics, Inc. 5400

Excitation Source: He II source

Source Energy: 40.8 eV

Source Strength: 30 W

Source Size: >5000 μm × >5000 μm

Incident Angle: 50°

Analyzer Type: spherical sector

Analyzer Pass Energy: 8.95 eV

Analyzer Resolution: 0.13 eV

Emission Angle: 90°

Total Signal Accumulation Time: 2646 s

Total Elapsed Time: 2920 s

Number of Scans: 66

Source Beam Size at Specimen Surface: >5000 μm × >5000 μm

Effective Detector Width: 0.13 eV

Analyzer Width: 1000 μm × 1000 μm

Analyzer Angular Acceptance Width: 14° × 14° at 25 eV

Comment: See footnote below the Spectral Features Table.