Epitaxial CrN(001) Grown and Analyzed *In situ* by XPS and UPS. II. Analysis of Ar^+ Sputter Etched Layers

Accession # 00624
Technique: XPS, UPS
Host Material: epitaxial CrN(001) thin film sputter etched
Instrument: Physical Electronics, Inc. 5400
Major Elements in Spectrum: Cr, N
Minor Elements in Spectrum: Ar
Printed Spectra: 5
Spectra in Electronic Record: 9
Spectral Category: comparison
Original Submission: 12/21/2000
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X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS) were used to study epitaxial CrN(001) grown *in situ* which were Ar^+ sputter etched. The films were deposited on MgO(001) at 650 °C in pure N_2 discharges maintained at a pressure of 5 mTorr (0.67) and shown to have a N/Cr ratio of 1.04±0.02 by Rutherford backscattering (RBS). The films were sputter etched with 3 keV Ar^+ at an angle of 40° to a constant nitrogen-to-chromium ratio. A Mg K_α x-ray source was used to obtain the XPS data, while the UPS data was generated by He I and He II UV radiation. The sputter etched films were found to have a N/Cr ratio, as determined by XPS, of 0.63, a decrease of 29% of that determined from the as-deposited surface. This indicates a preferential removal of nitrogen from the sputtered layers. © *2000 American Vacuum Society.*

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 sputter etched

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 Ar^+ sputter etched 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:** 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;

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and the photoelectron kinetic energy KE by $\theta = 7.5M \times \sqrt{PE/KE}$.

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: Mg K_α, 9.7°; He, 50°. Source-to-analyzer angles: Mg K_α, 54.7°; He, 60°. Emission angles: Mg K_α, 45°; He, 90°.

■ Ion Gun

Manufacturer and Model: Physical Electronics, Inc. 04-303

Energy: 3000 eV

Current: 0.0043 (mA/cm^2)

Current Measurement Method: Faraday cup

Sputtering Species: Ar

Spot Size (unrastered): 250 μm

Raster Size: 3000 μm $\times$ 3000 μm

Incident Angle: 40°

Polar Angle: 45°

Azimuthal Angle: 111°

Comment: The film was ion bombarded with a differentially pumped ion gun.

DATA ANALYSIS METHOD

Energy Scale Correction: The data did not require energy scale correction.

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 peak area. Peak areas were corrected, by dividing by the applicable sensitivity factor, and summed. Each corrected peak area was taken as a percentage of the total corrected peak area. (Software and sensitivity factors provided by Physical Electronics, Inc.)

ACKNOWLEDGMENTS

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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	Concen- tration (at. %)	Peak Assignment
00624-02	Cr $2p_{3/2}$	574.4	1.72	14979	2.427	64.7	CrN
00624-02	Cr $2p_{3/2}$	577.1	1.98	1405	···	···	CrN
00624-02[a]	···	579.3	8.00	7135	···	···	···
00624-02	Cr $2p_{1/2}$	583.8	1.96	7489	···	···	CrN
00624-02	Cr $2p_{1/2}$	586.5	2.15	702	···	···	CrN
00624-03	N $1s$	397.1	1.28	3397	0.477	35.3	CrN

Footnote to Spectrum 00624-04: The valence band photoelectron spectrum corresponds to the total density-of-states of CrN_x. The defective sputtered surface layer has no defined crystallographic orientation.

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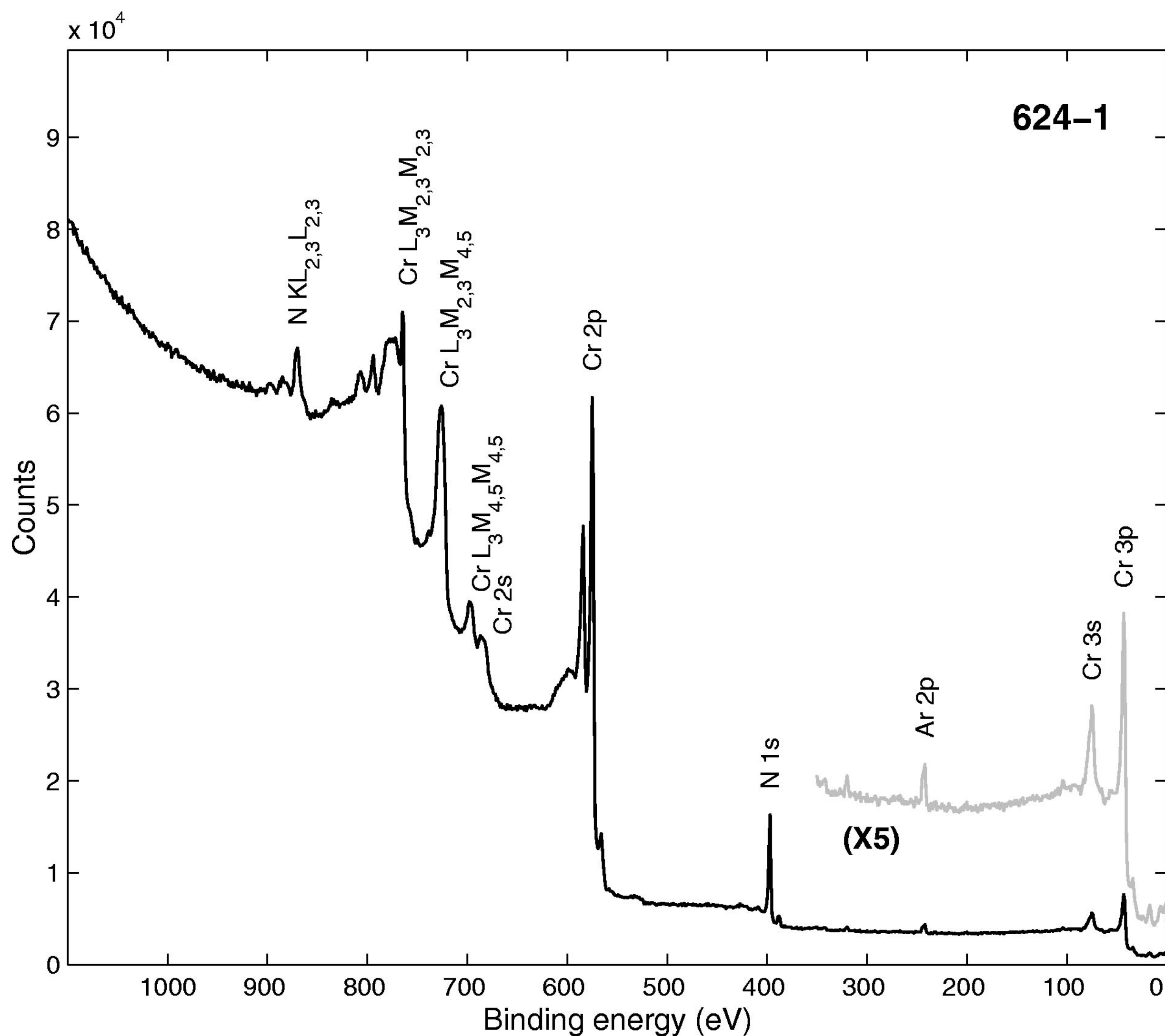
ANALYZER CALIBRATION TABLE

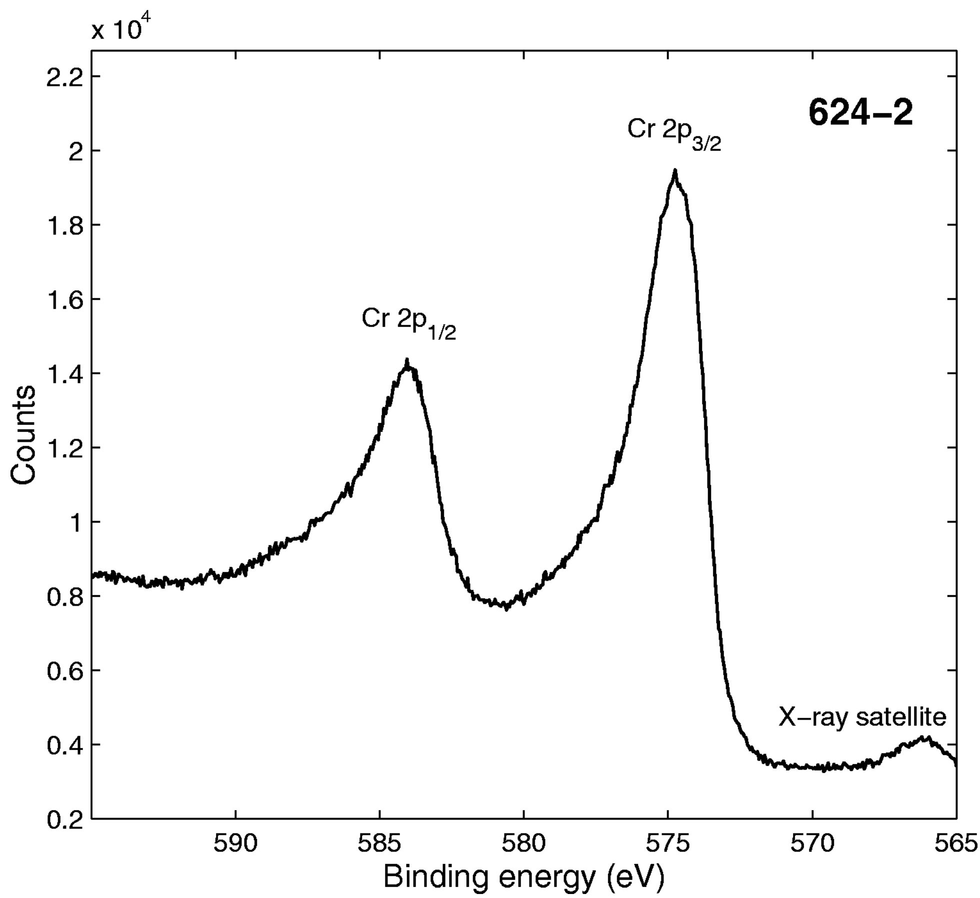
Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV-cts/s)	Sensitivity Factor	Concen- tration (at. %)	Peak Assignment
6	Au $4f_{7/2}$	84.0	1.03	34261	···	···	···
7	Cu $2p_{3/2}$	932.7	1.19	59588	···	···	···

GUIDE TO FIGURES					
Spectrum (Accession) #	**Spectral Region**	**Sample Voltage***	**Multiplier**	**Baseline**	**Comment #**
624-1	Survey	0	1	0	1
624-2	Cr $2p$	0	1	0	1
624-3	N $1s$	0	1	0	1
624-4	Valence band	0	1	0	2
624-5	Valence band	0	1	0	3
624-6 [NP]**	Au $4f$	0	1	0	1, 4
624-7 [NP]	Cu $2p_{3/2}$	0	1	0	1, 4

* 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. Mg K_α (1253.6 eV) excitation source
2. He I (21.2 eV) excitation source
3. He II (40.8 eV) excitation source
4. Calibration spectrum



Accession #	00624-01
Host Material	epitaxial CrN(001) thin film sputter etched
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 #:** 00624-02
- **Host Material:** epitaxial CrN(001) thin film sputter etched
- **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 $\times$ $>$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: 1683 s

Total Elapsed Time: 1805 s

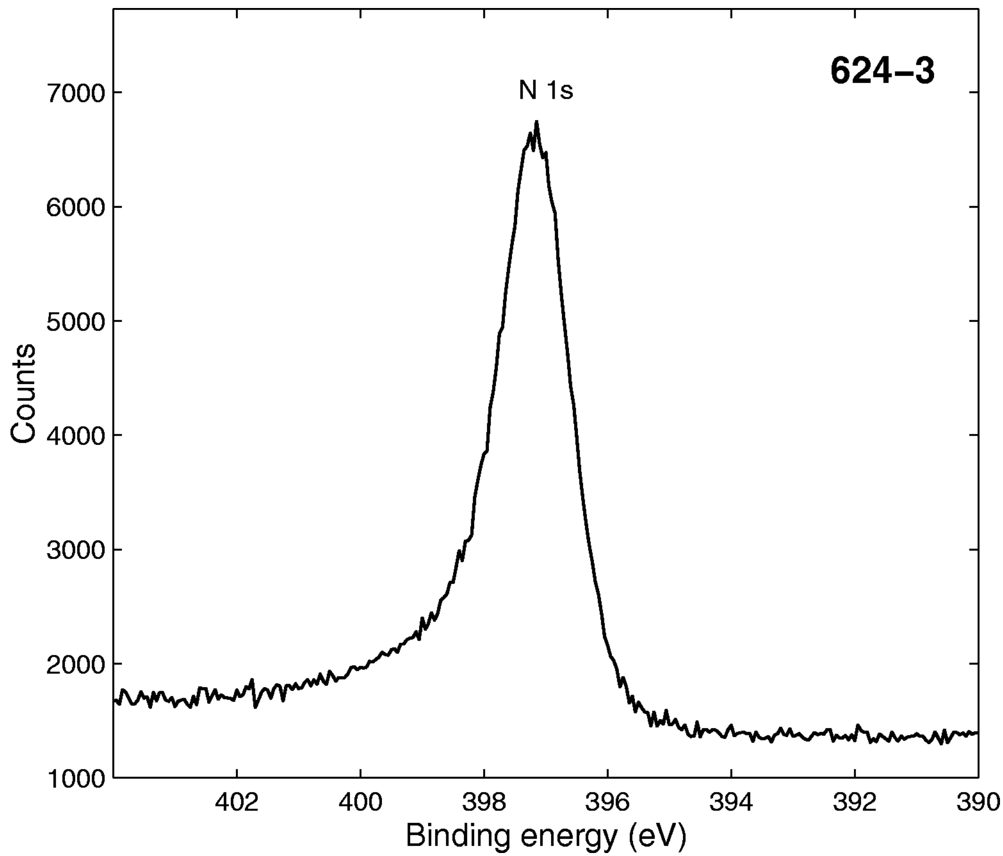
Number of Scans: 28

Source Beam Size at Specimen Surface: $>$25000 μm $\times$ $>$25000 μm

Effective Detector Width: 0.27 eV

Analyzer Width: 1414 μm $\times$ 1000 μm

Analyzer Angular Acceptance Width: 3° $\times$ 3° at 722 eV



- **Accession #:** 00624-03
- **Host Material:** epitaxial CrN(001) thin film sputter etched
- **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: 787 s

Total Elapsed Time: 909 s

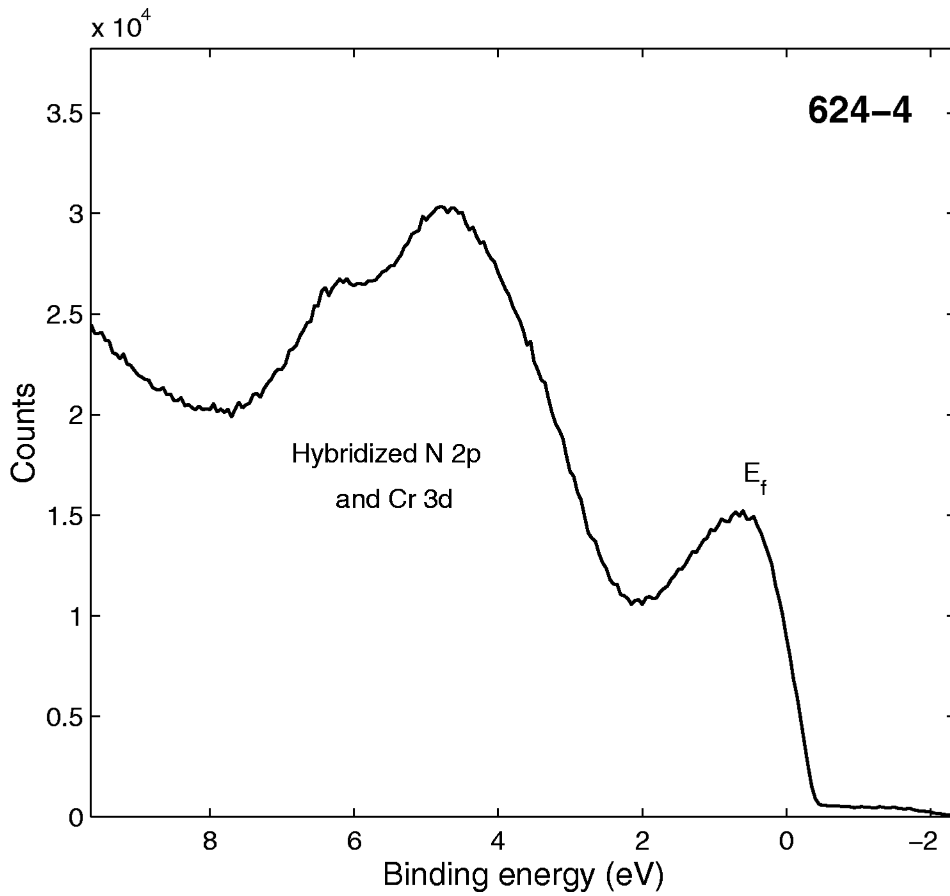
Number of Scans: 28

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 #:** 00624-04
- **Host Material:** epitaxial CrN(001) thin film sputter etched
- **Technique:** UPS
- **Spectral Region:** valence band

Instrument: Physical Electronics, Inc. 5400

Excitation Source: He I source

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

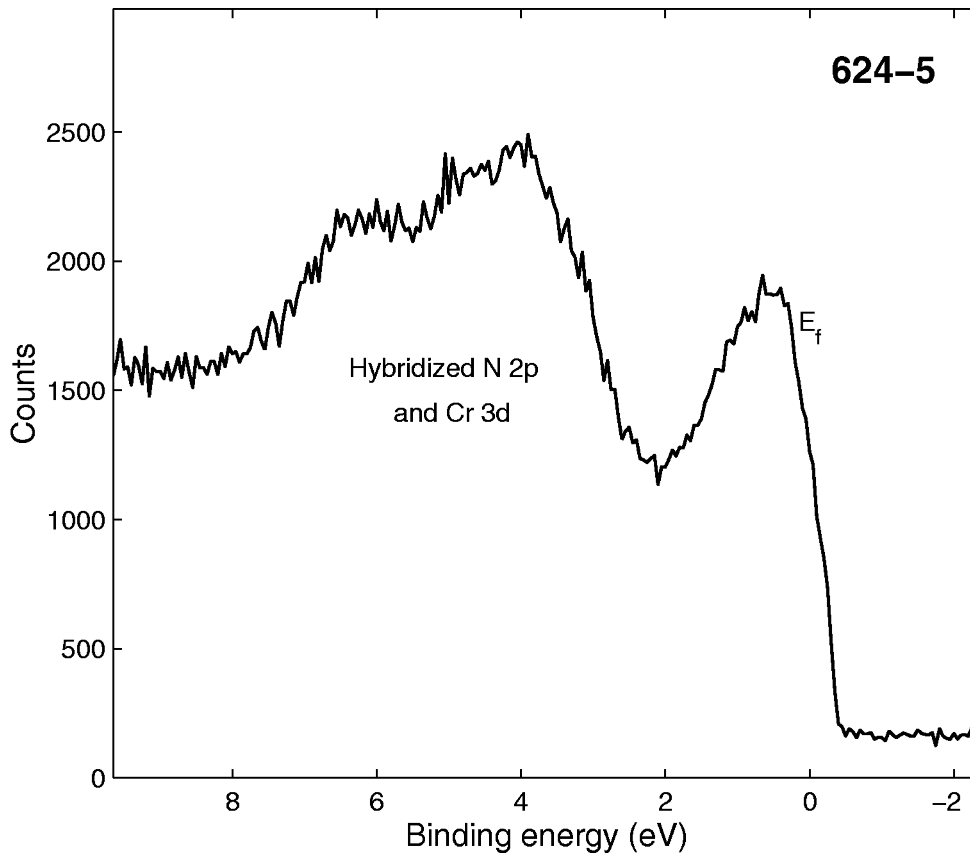
Source Beam Size at Specimen Surface: >5000 μm × >5000 μm

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 #:** 00624-05
- **Host Material:** epitaxial CrN(001) thin film sputter etched
- **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.