

# Epitaxial VN(001) Grown and Analyzed *In situ* by XPS and UPS. II. Analysis of Ar<sup>+</sup> Sputter Etched Layers

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X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS) were used to study epitaxial VN(001) layers grown *in situ* which were Ar<sup>+</sup> sputter etched. The films were deposited on MgO(001) at 650 °C in pure N<sub>2</sub> discharges maintained at a pressure of 5 mTorr (0.67 Pa) and shown to have a N/V ratio of 1.06±0.02 by Rutherford backscattering (RBS). The films were sputter etched with 3 keV Ar<sup>+</sup> at an angle of 40° to a constant nitrogen-to-vanadium ratio. A Mg K<sub>α</sub> 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/V ratio of 0.46, indicating a preferential removal of nitrogen. © 2000 American Vacuum Society.

**Keywords:** vanadium 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 VN(001) thin film sputter etched

**CAS Registry #:** 24646-85-3

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

**Chemical Name:** vanadium nitride

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

**Host Composition:** VN

**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<sup>+</sup> 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 VN(001) layers were grown in a multichamber UHV system. The turbomolecular-pumped growth chamber, having a base pressure of  $3 \times 10^{-9}$  Torr ( $4 \times 10^{-7}$  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  $1 \times 1$  RHEED patterns. The target, a 5-cm-diam water-cooled V disk (99.9%), was cleaned with a N<sub>2</sub> discharge prior to film growth. Depositions were carried out at  $T_s = 650$  °C in pure N<sub>2</sub> (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 23 nm/min. The total film thickness was 160 nm. The composition of the films was determined by RBS using 2 MeV He<sup>+</sup> at a scattering angle of 150°. Quantitative analysis was done using the surface height method (Ref. 2) yielding a N/V ratio of  $1.06 \pm 0.02$ .

**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:**  $< 3.0 \times 10^{-7}$  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  $\theta$ , 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  $\theta = 7.5M \times \sqrt{PE/KE}$ .

Accession # 00622

Technique: XPS, UPS

Host Material: epitaxial VN(001) thin film sputter etched

Instrument: Physical Electronics, Inc. 5400

Major Elements in Spectrum: V, N

Minor Elements in Spectrum: Ar

Printed Spectra: 5

Spectra in Electronic Record: 7

Spectral Category: comparison

Original Submission: 12/21/2000

Accepted for Publication: 1/23/2001

**Excitation Source Window:** 2  $\mu\text{m}$  aluminum window on Mg  $K_{\alpha}$

**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  $9 \times 10^{-6}$  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  $4 \times 10^{-6}$  Pa.

### ■ Geometry

**Incident Angle:** varies by spectrum

**Source to Analyzer Angle:** varies by spectrum

**Emission Angle:** 45°

**Specimen Azimuthal Angle:** 0°

**Acceptance Angle from Analyzer Axis:** 0°

**Comments:** Incident angles: Mg  $K_{\alpha}$  9.7°, He 50°. Source-to-analyzer angles: Mg  $K_{\alpha}$  54.7°, He 60°.

### ■ Ion Gun

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

**Energy:** 3000 eV

**Current:** 0.0043 (mA/cm<sup>2</sup>)

**Current Measurement Method:** Faraday cup

**Sputtering Species:** Ar

**Spot Size (unrastered):** 250  $\mu\text{m}$

**Raster Size:** 3000  $\mu\text{m} \times 3000 \mu\text{m}$

**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 energy scales of the UPS spectra were corrected by setting the Fermi energy ( $E_f$ ) to zero.

**Recommended Energy-Scale Shift:** Accession #s 622-04 and -05, 0.15 eV was added to the original energy scale.

**Intensity Scale Correction:** None.

**Peak Shape and Background Method:** A Shirley function was used for background corrections. Asymmetric Gaussian-Lorentzian line shapes were used to fit the V 2p and N 1s 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 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**

<b>Spectrum ID #</b>	<b>Element/ Transition</b>	<b>Peak Energy (eV)</b>	<b>Peak Width FWHM (eV)</b>	<b>Peak Area (eV-cts/s)</b>	<b>Sensitivity Factor</b>	<b>Concentration (at. %)</b>	<b>Peak Assignment</b>
00622-02	V $2p_{3/2}$	513.1	1.56	16653	2.116	68.3	VN
00622-02	V $2p_{3/2}$	516.7	3.30	1165	...	...	final-state relaxation satellite
00622-02	V $2p_{1/2}$	520.6	1.89	8326	...	...	VN
00622-02	V $2p_{1/2}$	524.3	2.94	582	...	...	final-state relaxation satellite
00622-03	N $1s$	397.4	1.23	2828	0.477	31.7	VN

**Footnote to Spectrum 00622-04:** The valence band photoelectron spectrum corresponds to the total density-of-states of VN<sub>x</sub>. The defective sputtered surface layer has no defined crystallographic orientation.

**Footnote to Spectrum 00622-05:** The valence band photoelectron spectrum corresponds to the total density-of-states of VN<sub>x</sub>. The defective sputtered surface layer has no defined crystallographic orientation.

**ANALYZER CALIBRATION TABLE**

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

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**GUIDE TO FIGURES**

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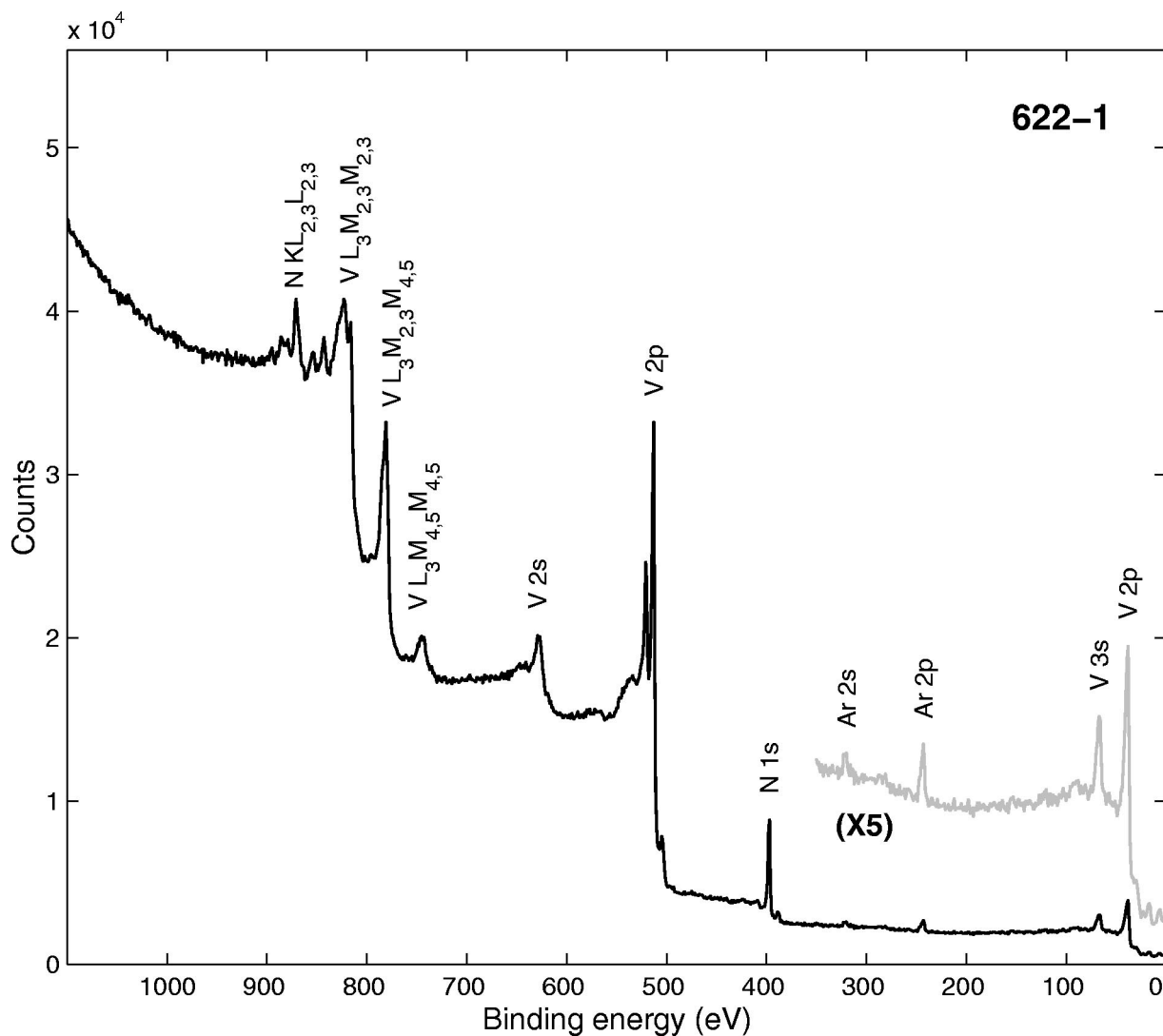
<b>Spectrum (Accession) #</b>	<b>Spectral Region</b>	<b>Sample Voltage*</b>	<b>Multiplier</b>	<b>Baseline</b>	<b>Comment #</b>
<b>622-1</b>	Survey	0	1	0	1
<b>622-2</b>	V 2 <i>p</i>	0	1	0	1
<b>622-3</b>	N 1 <i>s</i>	0	1	0	1
<b>622-4</b>	Valence band	-0.15	1	0	2
<b>622-5</b>	Valence band	-0.15	1	0	3
<b>622-6 [NP]**</b>	Au 4 <i>f</i>	0	1	0	1, 4
<b>622-7 [NP]</b>	Cu 2 <i>p</i> <sub>3/2</sub>	0	1	0	1, 4

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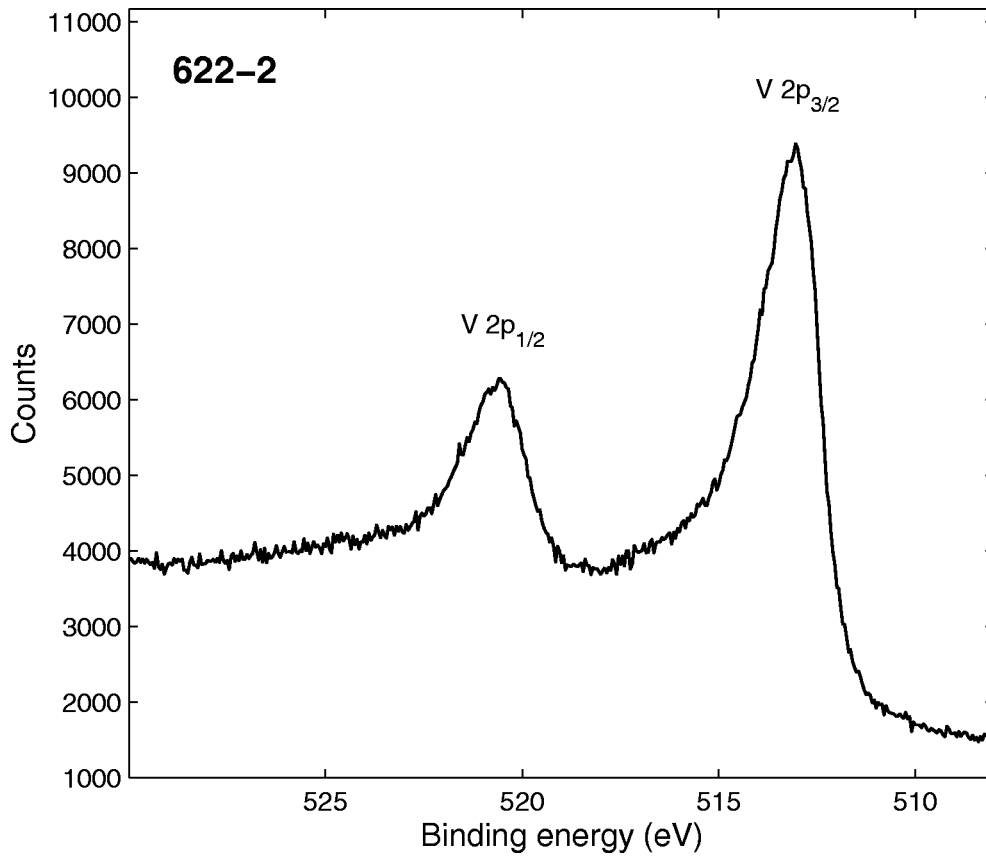
\* Inferred sample potential relative to spectrometer ground due to charging, flood gun, or other phenomena.

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

1. Mg  $K_{\alpha}$  (1253.6 eV) excitation source
2. He I (21.2 eV) excitation source
3. He II (40.8 eV) excitation source
4. Calibration spectrum



<b>Accession #</b>	<b>00622-01</b>
<b>Host Material</b>	epitaxial VN(001) thin film sputter etched
<b>Technique</b>	XPS
<b>Spectral Region</b>	survey
<b>Instrument</b>	Physical Electronics, Inc. 5400
<b>Excitation Source</b>	Mg $K_{\alpha}$
<b>Source Energy</b>	1253.6 eV
<b>Source Strength</b>	400 W
<b>Source Size</b>	>25000 $\mu\text{m}$ $\times$ >25000 $\mu\text{m}$
<b>Analyzer Type</b>	spherical sector
<b>Incident Angle</b>	9.7°
<b>Emission Angle</b>	45°
<b>Analyzer Pass Energy</b>	178.95 eV
<b>Analyzer Resolution</b>	2.7 eV
<b>Total Signal Accumulation Time</b>	220 s
<b>Total Elapsed Time</b>	238 s
<b>Number of Scans</b>	2
<b>Source Beam Size at Specimen Surface</b>	>25000 $\mu\text{m}$ $\times$ >25000 $\mu\text{m}$
<b>Effective Detector Width</b>	2.7 eV
<b>Analyzer Width</b>	1414 $\mu\text{m}$ $\times$ 1000 $\mu\text{m}$
<b>Analyzer Angular Acceptance Width</b>	24° $\times$ 24° at 150 eV



- **Accession #:** 00622-02
- **Host Material:** epitaxial VN(001) thin film sputter etched
- **Technique:** XPS
- **Spectral Region:** V 2p

Instrument: Physical Electronics, Inc. 5400

Excitation Source: Mg K<sub>α</sub>

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: 673 s

Total Elapsed Time: 739 s

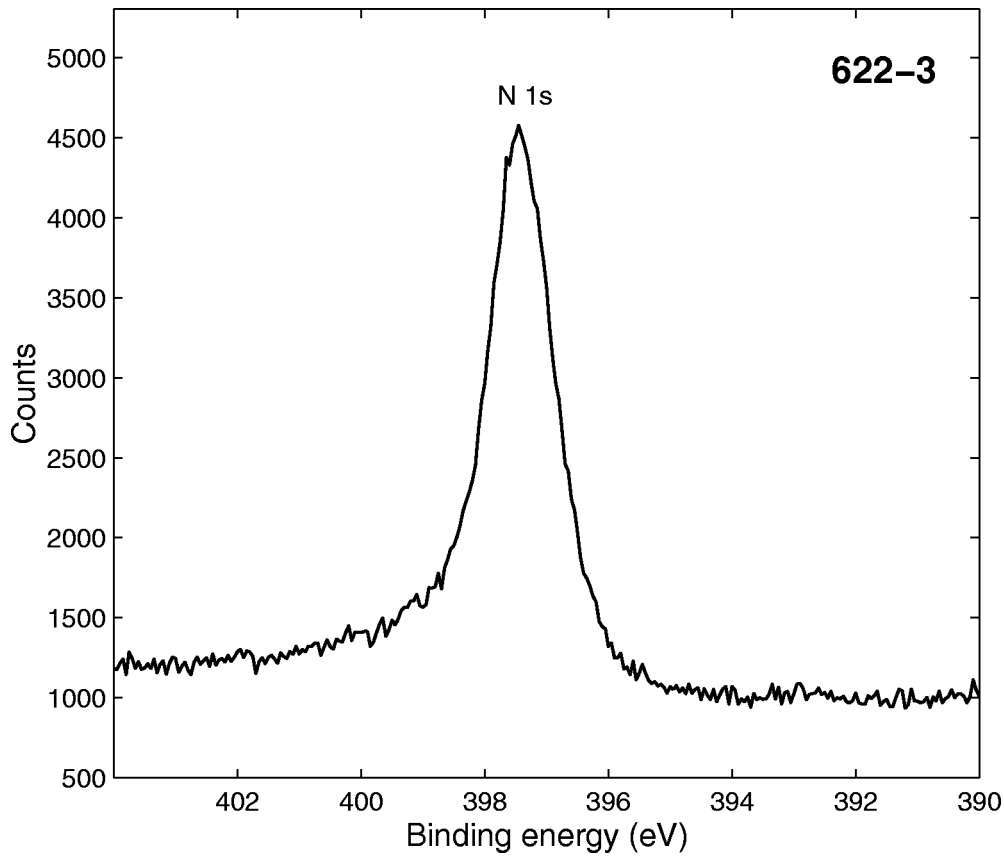
Number of Scans: 14

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 #:** 00622-03
- **Host Material:** epitaxial VN(001) thin film sputter etched
- **Technique:** XPS
- **Spectral Region:** N 1s

Instrument: Physical Electronics, Inc. 5400

Excitation Source: Mg  $K_{\alpha}$

Source Energy: 1253.6 eV

Source Strength: 400 W

Source Size: >25000  $\mu\text{m}$   $\times$  >25000  $\mu\text{m}$

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: 590 s

Total Elapsed Time: 684 s

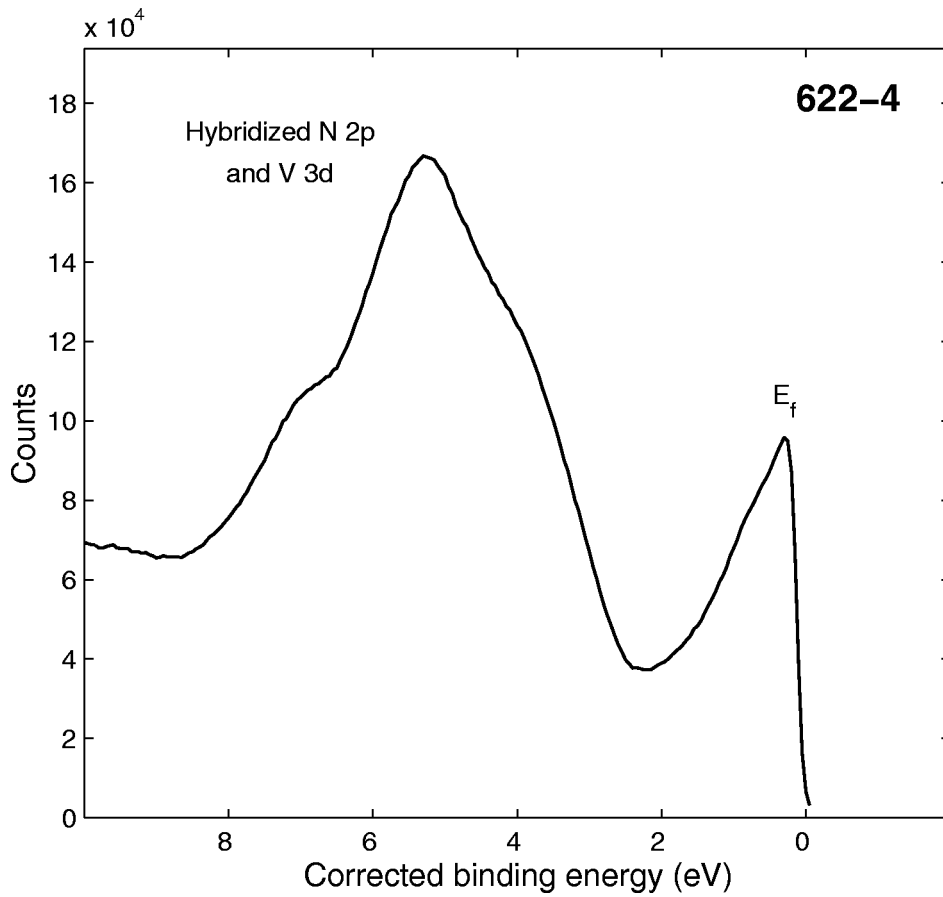
Number of Scans: 21

Source Beam Size at Specimen Surface: >25000  $\mu\text{m}$   $\times$  >25000  $\mu\text{m}$

Effective Detector Width: 0.27 eV

Analyzer Width: 1414  $\mu\text{m}$   $\times$  1000  $\mu\text{m}$

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



- **Accession #:** 00622-04
- **Host Material:** epitaxial VN(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:  $>5000 \mu\text{m} \times >5000 \mu\text{m}$

Incident Angle:  $50^\circ$

Analyzer Type: spherical sector

Analyzer Pass Energy: 8.95 eV

Analyzer Resolution: 0.13 eV

Emission Angle:  $45^\circ$

Total Signal Accumulation Time: 120 s

Total Elapsed Time: 150 s

Number of Scans: 5

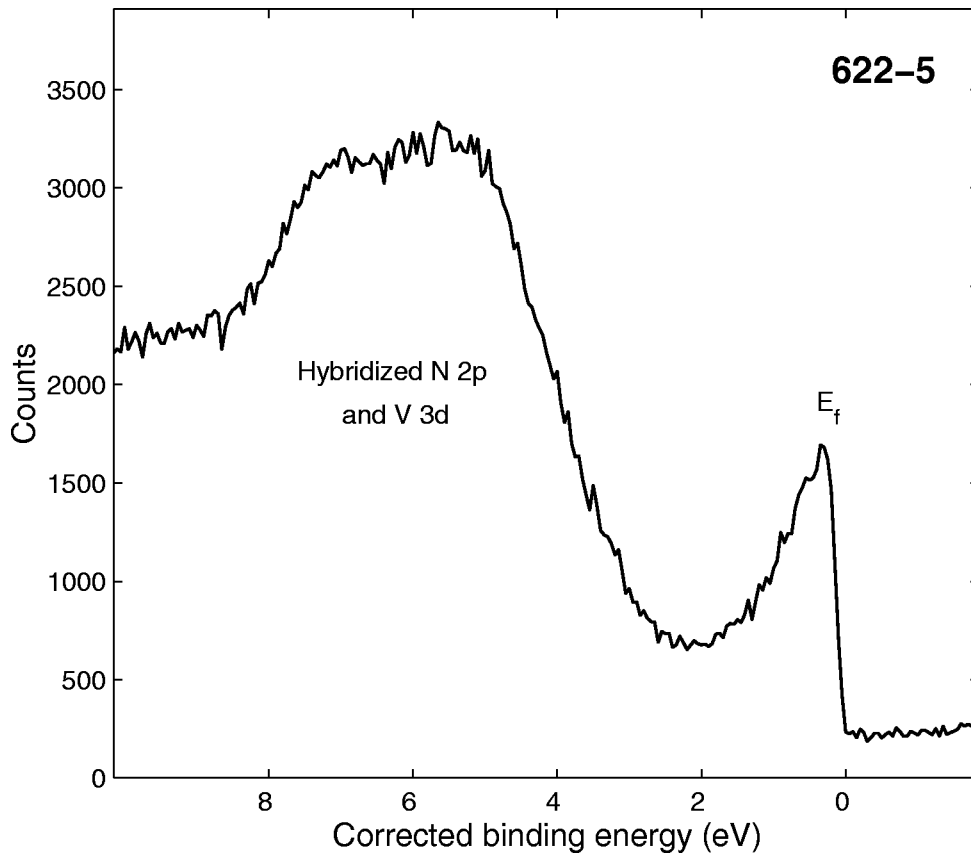
Source Beam Size at Specimen Surface:  $>5000 \mu\text{m} \times >5000 \mu\text{m}$

Effective Detector Width: 0.13 eV

Analyzer Width:  $1000 \mu\text{m} \times 1000 \mu\text{m}$

Analyzer Angular Acceptance Width:  $22^\circ \times 22^\circ$  at 9 eV

Comment: See footnote below the Spectral Features Table.



- **Accession #:** 00622-05
- **Host Material:** epitaxial VN(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  $\mu\text{m}$   $\times$  >5000  $\mu\text{m}$

Incident Angle: 50°

Analyzer Type: spherical sector

Analyzer Pass Energy: 8.95 eV

Analyzer Resolution: 0.13 eV

Emission Angle: 45°

Total Signal Accumulation Time: 2646 s

Total Elapsed Time: 3095 s

Number of Scans: 110

Source Beam Size at Specimen Surface: >5000  $\mu\text{m}$   $\times$  >5000  $\mu\text{m}$

Effective Detector Width: 0.13 eV

Analyzer Width: 1000  $\mu\text{m}$   $\times$  1000  $\mu\text{m}$

Analyzer Angular Acceptance Width: 14°  $\times$  14° at 25 eV

Comment: See footnote below the Spectral Features Table.