

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

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X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS) were used to characterize as-deposited epitaxial VN(001) layers grown *in situ*. 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). Mg K<sub>α</sub> and monochromatic Al K<sub>α</sub> x-ray sources were used to generate the XPS spectra, while the UPS data were generated by He I and He II UV radiation. Analysis of the results show that the VN(001) surfaces are free of O and C. The films were found to be stoichiometric in agreement with Rutherford backscattering spectroscopy (RBS) results, yielding a N/V ratio of 1.06±0.02. © 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 as-deposited

**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 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 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;

**Accession #** 00621

**Technique:** XPS, UPS

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

**Instrument:** Physical Electronics, Inc. 5400

**Major Elements in Spectrum:** V, 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

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

**Excitation Source Window:** 2  $\mu\text{m}$  aluminum window on Mg  $K_{\alpha}$ , none on other sources

**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:** varies by spectrum

**Specimen Azimuthal Angle:** 0°

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

**Comments:** Emission angles: Al  $K_{\alpha}$ , mono, and Mg  $K_{\alpha}$  45°, He 90°. Incident angles: Al  $K_{\alpha}$ , mono, 45°, Mg  $K_{\alpha}$  9.7°, He 50°. Source-to-analyzer angles: Al  $K_{\alpha}$ , mono, 90°, Mg  $K_{\alpha}$  54.7°, He 60°.

### DATA ANALYSIS METHOD

**Energy Scale Correction:** XPS binding energy scales for spectra collected with Al  $K_{\alpha}$ , mono, 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 621-01, -02 and -03, 0.3 eV is added to the original 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. Peaks 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	Concentration (at. %)	Peak Assignment
00621-02	V $2p_{3/2}$	513.3	1.07	1628	1.912	48.3	VN
00621-02	V $2p_{3/2}$	515.7	3.03	1240	...	...	final-state relaxation satellite
00621-02	V $2p_{1/2}$	520.8	1.92	813	...	...	VN
00621-02	V $2p_{1/2}$	523.3	3.60	620	...	...	final-state relaxation satellite
00621-03	N $1s$	397.2	0.94	1149	0.477	51.7	VN
00621-05	V $2p_{3/2}$	513.2	1.31	8458	2.116	49.6	VN
00621-05	V $2p_{3/2}$	515.5	3.6	7735	...	...	final-state relaxation satellite
00621-05	V $2p_{1/2}$	520.7	2.02	4228	...	...	VN
00621-05	V $2p_{1/2}$	523.0	4.56	3867	...	...	final-state relaxation satellite
00621-06	N $1s$	397.0	1.05	5566	0.477	50.4	VN

**Footnote to Spectrum 00621-07:** 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 00621-08:** 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	...	...	...

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**GUIDE TO FIGURES**

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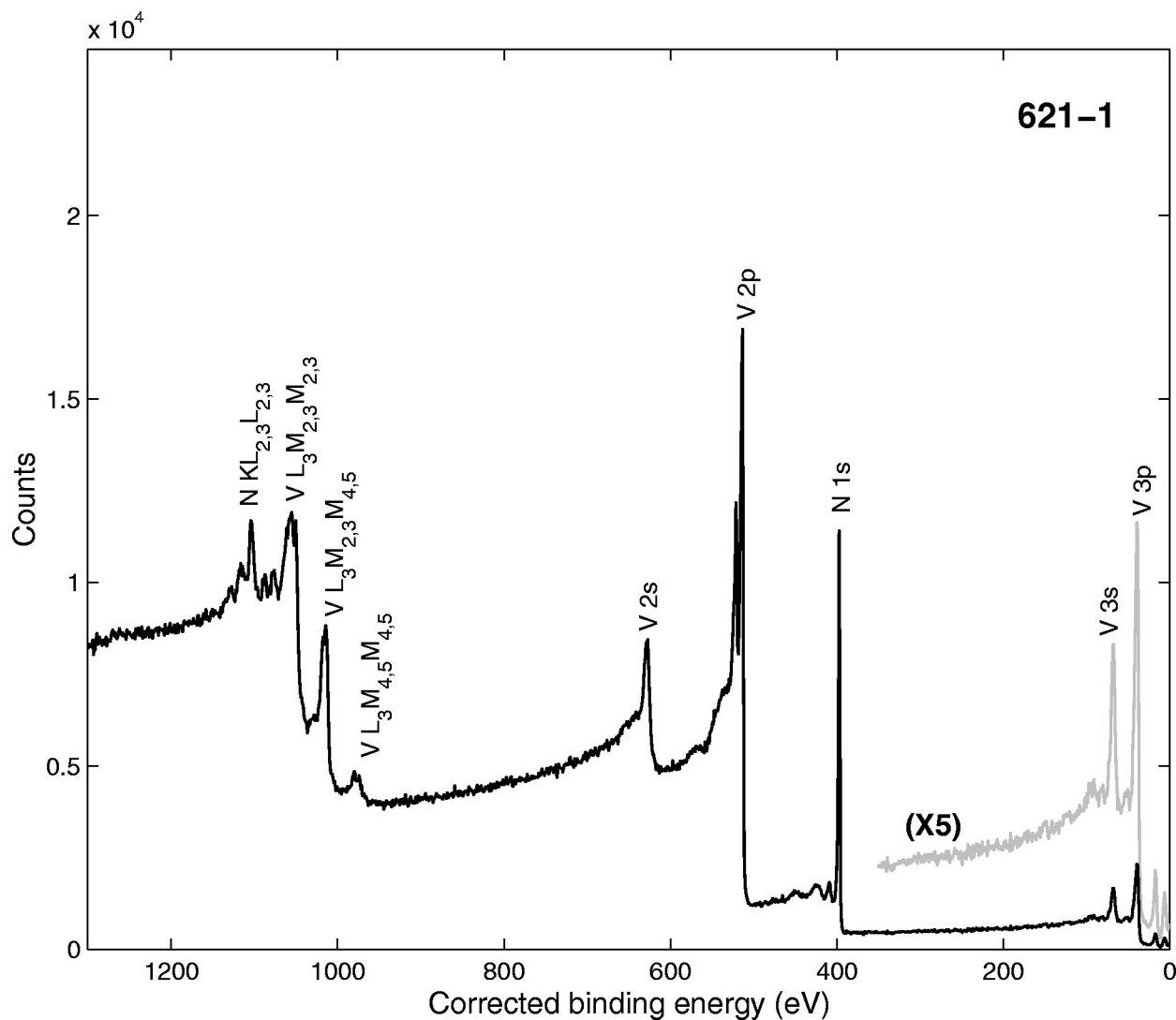
<b>Spectrum (Accession) #</b>	<b>Spectral Region</b>	<b>Sample Voltage*</b>	<b>Multiplier</b>	<b>Baseline</b>	<b>Comment #</b>
<b>621-1</b>	Survey	-0.3	1	0	1
<b>621-2</b>	V 2 <i>p</i>	-0.3	1	0	1
<b>621-3</b>	N 1 <i>s</i>	-0.3	1	0	1
<b>621-4</b>	Survey	0	1	0	2
<b>621-5</b>	V 2 <i>p</i>	0	1	0	2
<b>621-6</b>	N 1 <i>s</i>	0	1	0	2
<b>621-7</b>	Valence band	0	1	0	3
<b>621-8</b>	Valence band	0	1	0	4
<b>621-9 [NP]**</b>	Au 4 <i>f</i>	-0.3	1	0	1, 5
<b>621-10 [NP]</b>	Cu 2 <i>p</i> <sub>3/2</sub>	-0.3	1	0	1, 5
<b>621-11 [NP]</b>	Au 4 <i>f</i>	0	1	0	2, 5
<b>621-12 [NP]</b>	Cu 2 <i>p</i> <sub>3/2</sub>	0	1	0	2, 5

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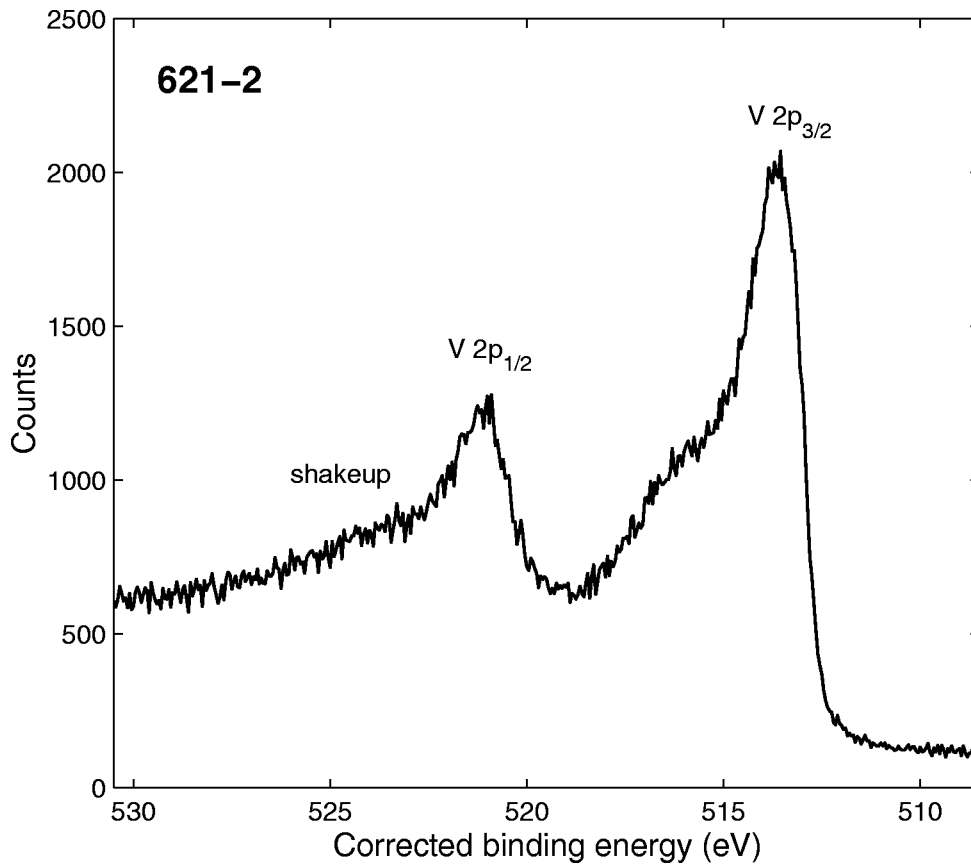
\* Inferred sample potential relative to spectrometer ground due to charging, flood gun, or other phenomena.

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

1. Monochromated Al  $K_{\alpha}$  (1486.6 eV) excitation source
2. Mg  $K_{\alpha}$  (1253.6 eV) excitation source
3. He I (21.2 eV) excitation source
4. He II (40.8 eV) excitation source
5. Calibration spectrum



<b>Accession #</b>	<b>00621-01</b>
<b>Host Material</b>	epitaxial VN(001) thin film as-deposited
<b>Technique</b>	XPS
<b>Spectral Region</b>	survey
<b>Instrument</b>	Physical Electronics, Inc. 5400
<b>Excitation Source</b>	Al $K_{\alpha}$ monochromatic
<b>Source Energy</b>	1486.6 eV
<b>Source Strength</b>	500 W
<b>Source Size</b>	2000 $\mu\text{m}$ $\times$ 2000 $\mu\text{m}$
<b>Analyzer Type</b>	spherical sector
<b>Incident Angle</b>	45°
<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>	1041 s
<b>Total Elapsed Time</b>	1083 s
<b>Number of Scans</b>	8
<b>Source Beam Size at Specimen Surface</b>	2828 $\mu\text{m}$ $\times$ 2000 $\mu\text{m}$
<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>	22° $\times$ 22° at 190 eV



- **Accession #:** 00621-02
- **Host Material:** epitaxial VN(001) thin film as-deposited
- **Technique:** XPS
- **Spectral Region:** V 2p

Instrument: Physical Electronics, Inc. 5400

Excitation Source: Al K<sub>α</sub> 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: 1058 s

Total Elapsed Time: 1156 s

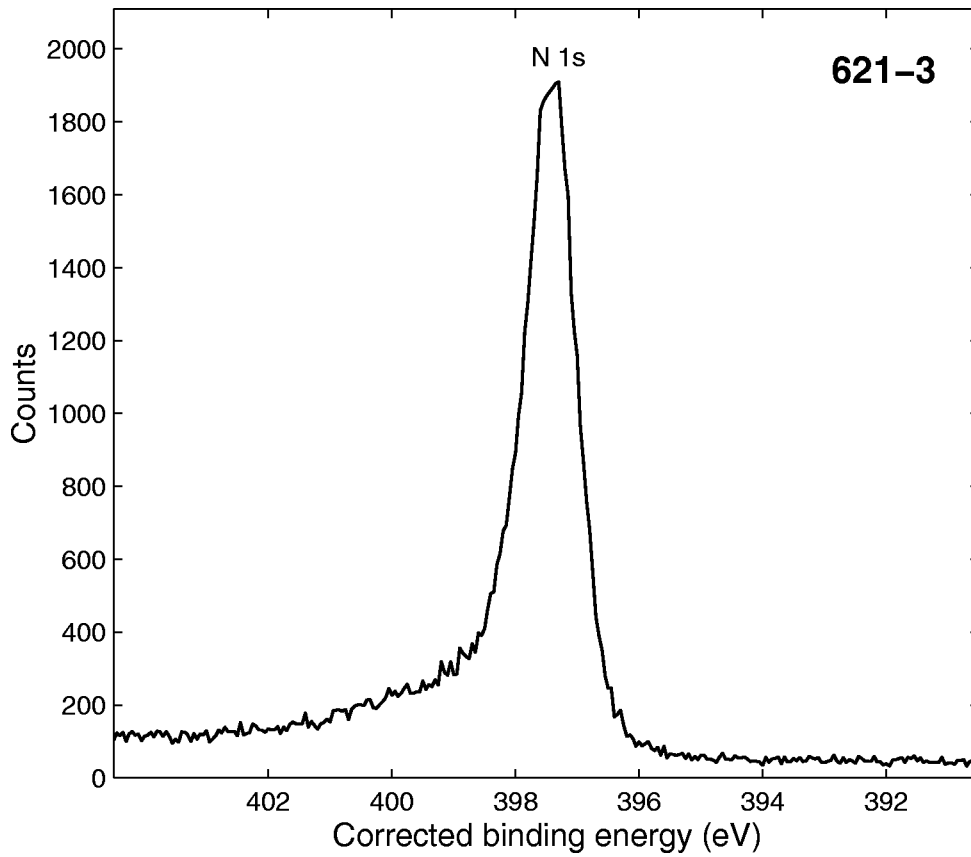
Number of Scans: 22

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 #:** 00621-03
- **Host Material:** epitaxial  
VN(001) thin film as-deposited
- **Technique:** XPS
- **Spectral Region:** N 1s

Instrument: Physical Electronics,  
Inc. 5400

Excitation Source: Al  $K_{\alpha}$   
monochromatic

Source Energy: 1486.6 eV

Source Strength: 500 W

Source Size: 2000  $\mu\text{m}$   $\times$  2000  $\mu\text{m}$

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:  
618 s

Total Elapsed Time: 716 s

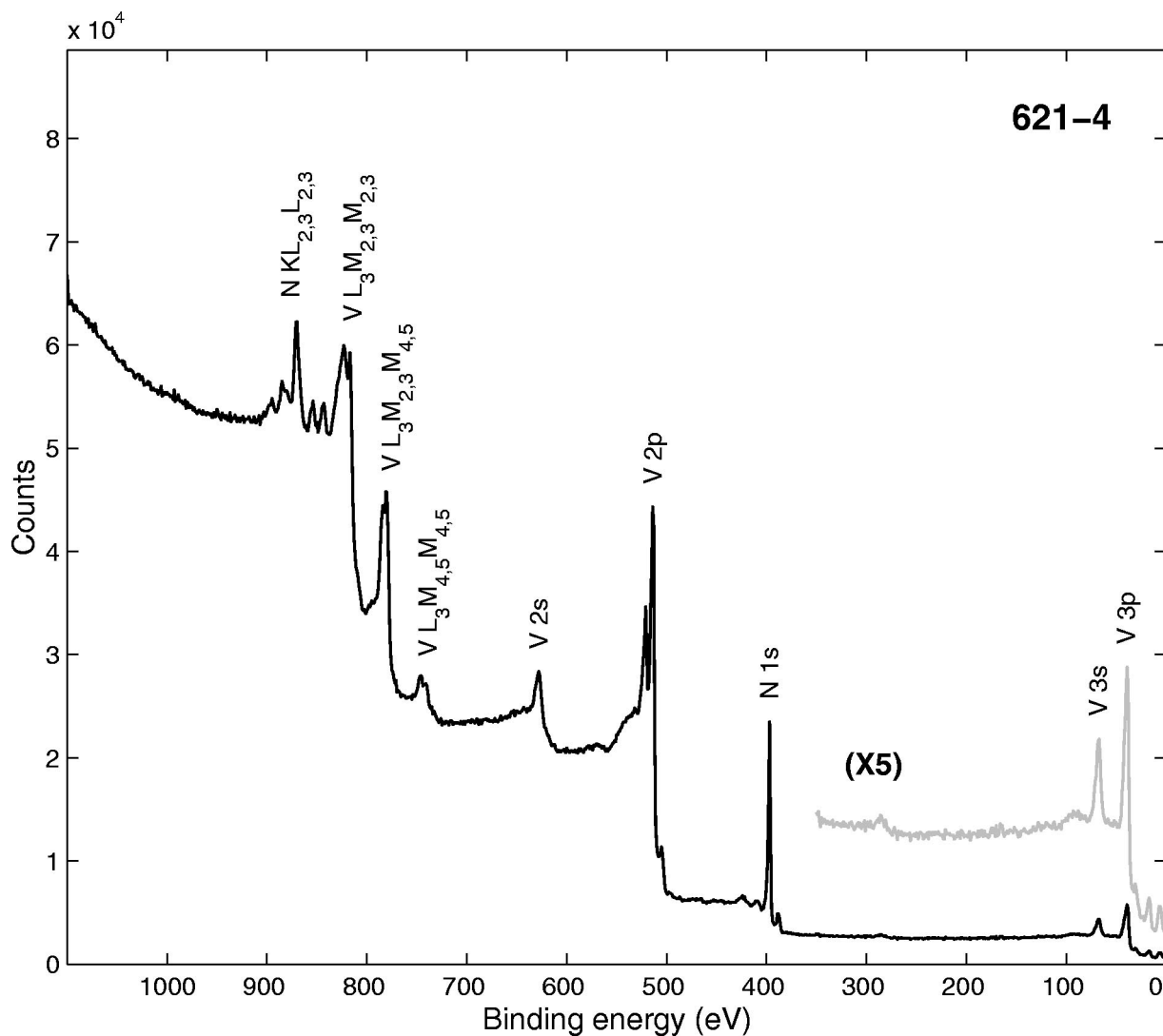
Number of Scans: 22

Source Beam Size at Specimen  
Surface: 2828  $\mu\text{m}$   $\times$  2000  $\mu\text{m}$

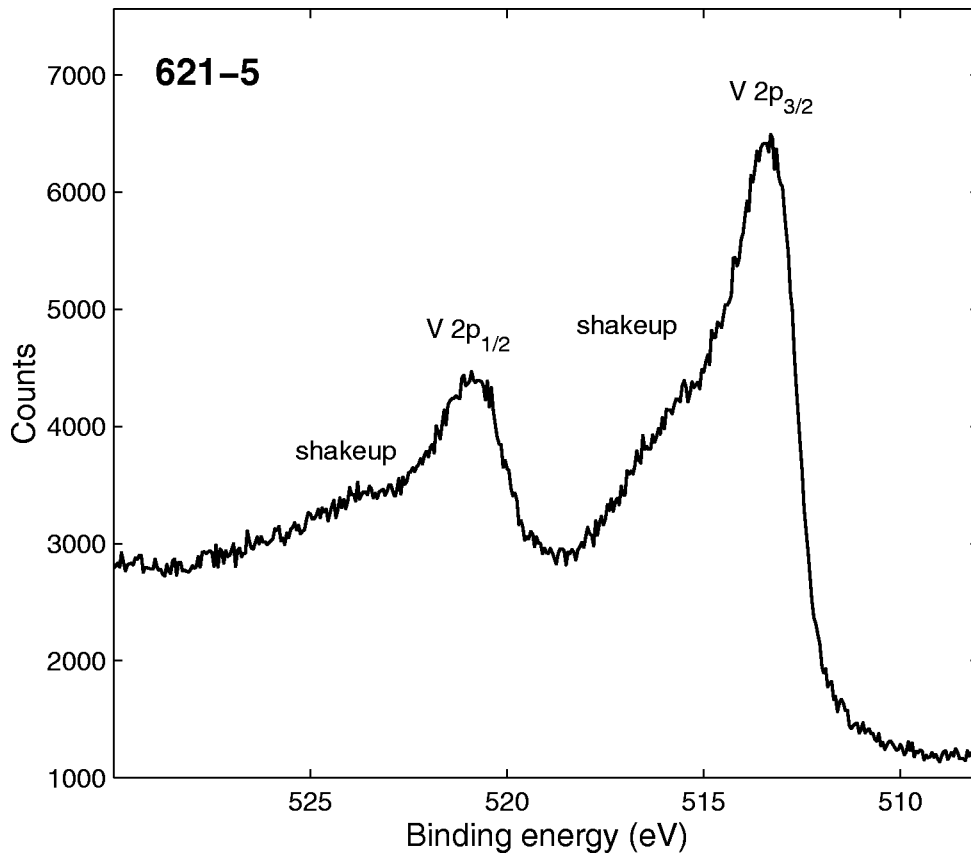
Effective Detector Width: 0.27 eV

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

Analyzer Angular Acceptance Width:  
3°  $\times$  3° at 955 eV



<b>Accession #</b>	<b>00621-04</b>
<b>Host Material</b>	epitaxial VN(001) thin film as-deposited
<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>	330 s
<b>Total Elapsed Time</b>	347 s
<b>Number of Scans</b>	3
<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 #:** 00621-05
- **Host Material:** epitaxial VN(001) thin film as-deposited
- **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: 577 s

Total Elapsed Time: 635 s

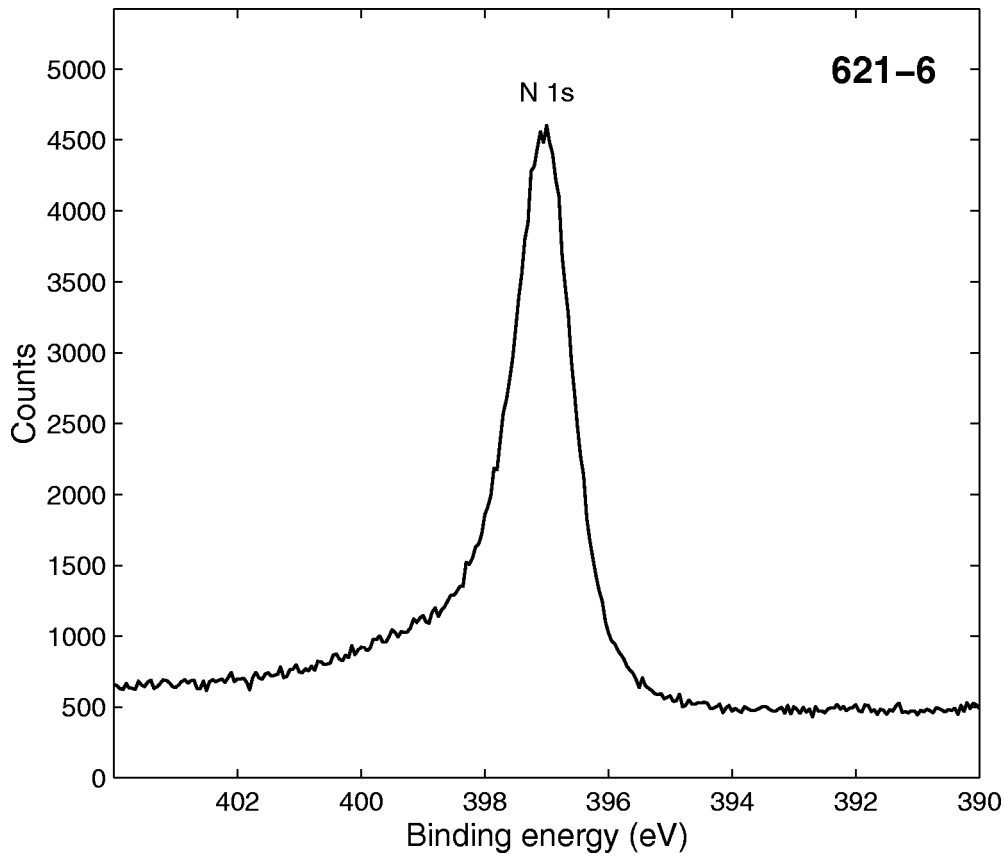
Number of Scans: 12

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 #:** 00621-06
- **Host Material:** epitaxial VN(001) thin film as-deposited
- **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: 337 s

Total Elapsed Time: 395 s

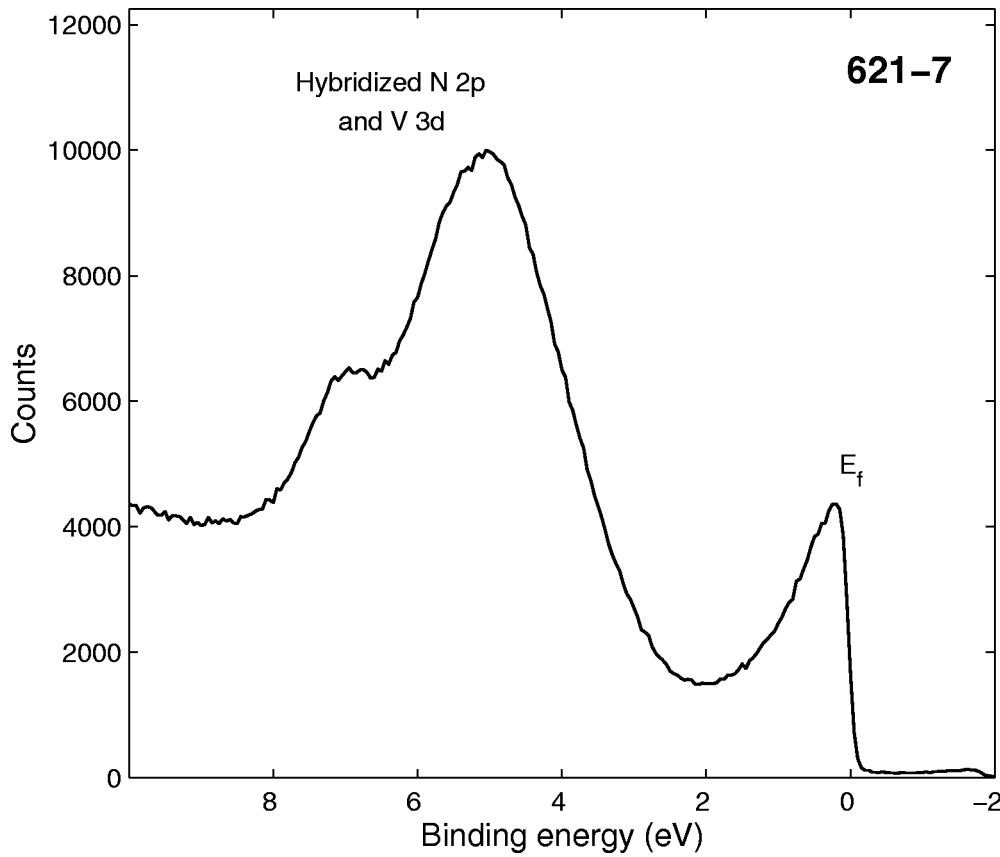
Number of Scans: 12

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

Effective Detector Width: 0.27 eV

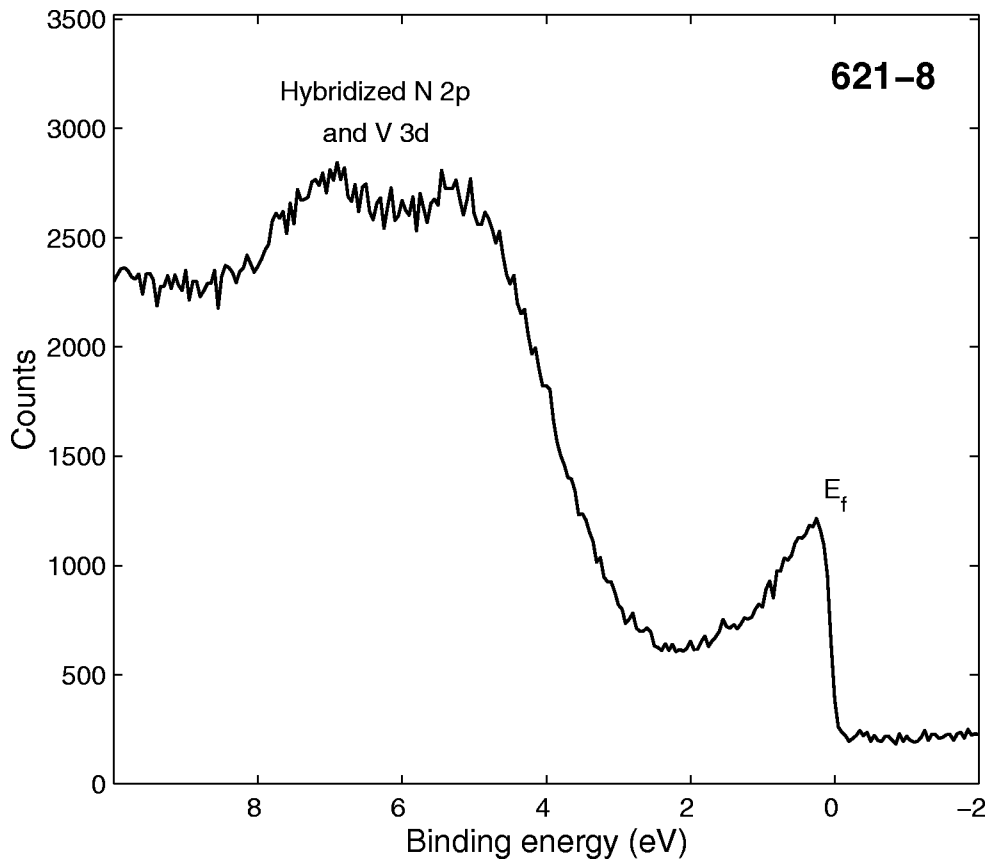
Analyzer Width: 1414  $\mu\text{m}$   $\times$  1000  $\mu\text{m}$

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



- **Accession #:** 00621-07
- **Host Material:** epitaxial VN(001) thin film as-deposited
- **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:  $90^\circ$   
 Total Signal Accumulation Time: 72 s  
 Total Elapsed Time: 142 s  
 Number of Scans: 3  
 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 #: 00621-08
- Host Material: epitaxial VN(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:  $>5000 \mu\text{m} \times >5000 \mu\text{m}$

Incident Angle:  $50^\circ$

Analyzer Type: spherical sector

Analyzer Pass Energy: 8.95 eV

Analyzer Resolution: 0.13 eV

Emission Angle:  $90^\circ$

Total Signal Accumulation Time: 1591 s

Total Elapsed Time: 2646 s

Number of Scans: 66

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:  $14^\circ \times 14^\circ$  at 25 eV

Comment: See footnote below the Spectral Features Table.