Epitaxial VN(001) Grown and Analyzed In situ by XPS and UPS. II. Analysis of Ar+ 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+ sputter etched. The films were deposited on MgO(001) at 650 °C in pure N2 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+ at an angle of 40° to a constant nitrogen-to-vanadium ratio. A Mg Kα 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+ 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

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 × 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 × 5 × 0.5 mm) were annealed at \(T_a = 850\) °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 V disk (99.99%), was cleaned with a N2 discharge prior to film growth. Depositions were carried out at \(T_s = 650\) °C in pure N2 (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\(^+\) 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 ± 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: <3.0×10\(^{-7}\) 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 \((T=E^{\theta})\): \(N=0\)

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 \(\theta = 7.5M \times \sqrt{PE/KE}\).
Excitation Source Window: 2 μm aluminum window on Mg Kα
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} \text{ 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} \text{ 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 Kα 9.7°, He 50°. Source-to-analyzer angles: Mg Kα 54.7°, He 60°.

Ion Gun

Manufacturer and Model: Physical Electronics, Inc. 04-303A
Energy: 3000 eV
Current: 0.0043 (mA/cm²)
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 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 622-05, 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

### SPECTRAL FEATURES TABLE

<table>
<thead>
<tr>
<th>Spectrum ID #</th>
<th>Element/Transition</th>
<th>Peak Energy (eV)</th>
<th>Peak Width FWHM (eV)</th>
<th>Peak Area (eV-cts/s)</th>
<th>Sensitivity Factor</th>
<th>Concentration (at. %)</th>
<th>Peak Assignment</th>
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<tr>
<td>00622-02</td>
<td>V 2(^{p}_{3/2})</td>
<td>513.1</td>
<td>1.56</td>
<td>16653</td>
<td>2.116</td>
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<td>3.30</td>
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<td>1.89</td>
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<td>00622-03</td>
<td>N 1(^{s})</td>
<td>397.4</td>
<td>1.23</td>
<td>2828</td>
<td>0.477</td>
<td>31.7</td>
<td>VN</td>
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</tbody>
</table>

Footnote to Spectrum 00622-04: The valence band photoelectron spectrum corresponds to the total density-of-states of VN\(_x\). 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\(_x\). The defective sputtered surface layer has no defined crystallographic orientation.

### ANALYZER CALIBRATION TABLE

<table>
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<tr>
<th>Spectrum ID #</th>
<th>Element/Transition</th>
<th>Peak Energy (eV)</th>
<th>Peak Width FWHM (eV)</th>
<th>Peak Area (eV-cts/s)</th>
<th>Sensitivity Factor</th>
<th>Concentration (at. %)</th>
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<td>Spectrum (Accession) #</td>
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<td>Multiplier</td>
<td>Baseline</td>
<td>Comment #</td>
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<td>1, 4</td>
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</tbody>
</table>

* 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 Kα (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 # 00622-01

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

Technique, XPS survey

Spectral Region, Physical Electronics, Inc. 5400

Instrument, Mg Kα

Excitation Source, 1253.6 eV

Source Energy, 400 W

Source Strength, >25000 μm × >25000 μm

Source Size, spherical sector

Analyzer Type, 9.7°

Incident Angle, 45°

Emission Angle, 178.95 eV

Analyzer Pass Energy, 2.7 eV

Analyzer Resolution, 220 s

Total Signal Accumulation Time, 238 s

Total Elapsed Time, 2 scans

Number of Scans, >25000 μm × >25000 μm

Source Beam Size at Specimen Surface, 2.7 eV

Effective Detector Width, 1414 μm × 1000 μm

Analyzer Width, 24° × 24° at 150 eV

Analyzer Angular Acceptance Width
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_{\alpha}
Source Energy: 1253.6 eV
Source Strength: 400 W
Source Size: 25000 \mu m \times 25000 \mu 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: 673 s
Total Elapsed Time: 739 s
Number of Scans: 14
Source Beam Size at Specimen Surface: 25000 \mu m \times 25000 \mu m
Effective Detector Width: 0.27 eV
Analyzer Width: 1414 \mu m \times 1000 \mu m
Analyzer Angular Acceptance Width: 3° \times 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 Kα
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: 590 s
Total Elapsed Time: 684 s
Number of Scans: 21
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 #: 00622-04
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°
Analyzer Type: spherical sector
Analyzer Pass Energy: 8.95 eV
Analyzer Resolution: 0.13 eV
Emission Angle: 45°
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° × 22° 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 μm x >5000 μm
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 μm x >5000 μm
Effective Detector Width: 0.13 eV
Analyzer Width: 1000 μm x 1000 μm
Analyzer Angular Acceptance Width: 14° x 14° at 25 eV
Comment: See footnote below the Spectral Features Table.