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

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 TiN(001) layers grown in situ. The films were deposited by ultrahigh vacuum reactive magnetron sputtering on MgO(001) at 850 °C in pure N₂ discharges maintained at a pressure of 5 mTorr (0.67 Pa). Mg Kα and monochromatic Al Kα x-ray sources were used to obtain the XPS spectra, while the UPS data was generated by He I and He II UV radiation. The spectra show that the TiN(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/Ti ratio of 1.02 ± 0.02. © 2000 American Vacuum Society.

Keywords: titanium nitride; magnetron sputtering; hard coatings; transition metal nitrides

PACS: 82.80.Pv, 81.05.Je, 81.15.Cd, 61.50.Nw

SPECIMEN DESCRIPTION

Host Material: epitaxial TiN(001) thin film as-deposited
CAS Registry #: 25583-20-4
Host Material Characteristics: homogeneous; solid; single crystal; conductor; inorganic compound; thin film
Chemical Name: titanium nitride
Source: epitaxially grown in situ on MgO(001) by ultrahigh vacuum reactive magnetron sputtering
Host Composition: TiN
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
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 TiN(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 Tₐ = 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 Ti disk (99.999%), was cleaned with a N₂ discharge prior to film growth. Depositions were carried out at Tₓ = 800 °C in pure N₂ (99.999%) 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 8 nm/min. The total film thickness was 40 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/Ti ratio of 1.02 ± 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 (I=EI): 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 $\theta = 7.5M \times \sqrt{PE/KE}$. 

Excitation Source Window: 2 μm aluminum window on Mg $K_\alpha$ 
Signal Mode: multichannel direct 

**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° 

**Source Analysis Method**

Energy Scale Correction: XPS binding energy scales for spectra collected with Al $K_\alpha$, mono, were corrected using Au 4f7/2=84.0 and Cu 2p3/2=932.7. All other data did not require energy scale correction.

Recommended Energy-Scale Shift: Accession #s 625-2, 625-2 and 625-3, 0.3 eV is added to the original energy scale.

Peak Shape and Background Method: A Shirley function was used for background corrections. An asymmetric Gaussian–Lorentzian line shape was used to fit the Ti 2p region. A Gaussian–Lorentzian line shape was used to fit the N 1s region. (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 and sensitivity factors 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**


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**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>00625-02</td>
<td>Ti 2p3/2</td>
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<tr>
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<td>N 1s</td>
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Footnote to Spectrum 00625-07: 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) and sharp peaks from photoelectrons with momentum conserved along the (001) direction.

The peaks at 2.5, 3.8, and 6.7 eV are due to photoelectrons from the $\Delta_2$, $\Delta_4$, and $\Delta_5$ bands, respectively, and correspond to momentum-conserving transitions from valence bands, between the $\Gamma$ and X points in the Brillouin zone to final states 15–20 eV above the Fermi level. The peak at 14.2 eV is due to a high density of final states at $\Gamma$, 7 eV above $E_F$.

Footnote to Spectrum 00625-08: 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 I spectrum closely resembles the total density-of-states (DOS).
## ANALYZER CALIBRATION 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>
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<td>1.01</td>
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<td>1.23</td>
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## GUIDE TO FIGURES

<table>
<thead>
<tr>
<th>Spectrum (Accession) #</th>
<th>Spectral Region</th>
<th>Sample Voltage*</th>
<th>Multiplier</th>
<th>Baseline</th>
<th>Comment #</th>
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<tbody>
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<td>625-1</td>
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<td>625-7</td>
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<td>1</td>
<td>0</td>
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<tr>
<td>625-8</td>
<td>Valence band</td>
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<td>1</td>
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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 Kα (1486.6 eV) excitation source
2. Mg Kα (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 # 00625-01

Host Material
epitaxial TiN(001) thin film as-deposited

Technique
XPS survey

Spectral Region
survey

Instrument
Physical Electronics, Inc. 5400

Excitation Source
Al $K_{\alpha}$ monochromatic

Source Energy
1486.6 eV

Source Strength
500 W

Source Size
2000 $\mu$m $\times$ 2000 $\mu$m

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
1041 s

Total Elapsed Time
1083 s

Number of Scans
8

Source Beam Size at Specimen Surface
2828 $\mu$m $\times$ 2000 $\mu$m

Effective Detector Width
2.7 eV

Analyzer Width
1414 $\mu$m $\times$ 1000 $\mu$m

Analyzer Angular Acceptance Width
22° $\times$ 22° at 190 eV
Accession #: 00625-02
Host Material: epitaxial TiN(001) thin film as-deposited
Technique: XPS
Spectral Region: Ti 2p

Instrument: Physical Electronics, Inc. 5400
Excitation Source: Al K$_\alpha$ monochromatic
Source Energy: 1486.6 eV
Source Strength: 500 W
Source Size: 2000 $\mu$m $\times$ 2000 $\mu$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: 651 s
Total Elapsed Time: 713 s
Number of Scans: 13
Source Beam Size at Specimen Surface: 2828 $\mu$m $\times$ 2000 $\mu$m
Effective Detector Width: 0.27 eV
Analyzer Width: 1414 $\mu$m $\times$ 1000 $\mu$m
Analyzer Angular Acceptance Width: 3° $\times$ 3° at 955 eV
Comment: The 2p$_{3/2}$ and 2p$_{1/2}$ lines show intense shake-up satellites.
Accession #: 00625-03
Host Material: epitaxial TiN(001) thin film as-deposited
Technique: XPS
Spectral Region: N 1s

Instrument: Physical Electronics, Inc. 5400
Excitation Source: Al Kα 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: 365 s
Total Elapsed Time: 427 s
Number of Scans: 13
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
<table>
<thead>
<tr>
<th>Accession #</th>
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<td>epitaxial TiN(001) thin film as-deposited</td>
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<tr>
<td>Technique</td>
<td>XPS</td>
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<tr>
<td>Spectral Region</td>
<td>survey</td>
</tr>
<tr>
<td>Instrument</td>
<td>Physical Electronics, Inc. 5400</td>
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<tr>
<td>Excitation Source</td>
<td>Mg $K_a$</td>
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<td>Source Energy</td>
<td>1253.6 eV</td>
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<tr>
<td>Source Strength</td>
<td>400 W</td>
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<tr>
<td>Source Size</td>
<td>$&gt;25000 \mu m \times &gt;25000 \mu m$</td>
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<tr>
<td>Incident Angle</td>
<td>9.7°</td>
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<tr>
<td>Analyzer Type</td>
<td>spherical sector</td>
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<tr>
<td>Analyzer Pass Energy</td>
<td>178.95 eV</td>
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<td>Analyzer Resolution</td>
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<tr>
<td>Emission Angle</td>
<td>45°</td>
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<td>Total Signal Accumulation Time</td>
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<td>Total Elapsed Time</td>
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<td>Number of Scans</td>
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<td>Source Beam Size at Specimen Surface</td>
<td>$&gt;25000 \mu m \times &gt;25000 \mu m$</td>
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<tr>
<td>Effective Detector Width</td>
<td>2.7 eV</td>
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<tr>
<td>Analyzer Width</td>
<td>1414 $\mu m \times 1000 \mu m$</td>
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<td>Analyzer Angular Acceptance Width</td>
<td>$24° \times 24°$ at 150 eV</td>
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Accession #: 00625-05
Host Material: epitaxial TiN(001) thin film as-deposited
Technique: XPS
Spectral Region: Ti 2p

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: 1503 s
Total Elapsed Time: 1633 s
Number of Scans: 30
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
Comment: The 2p½ and 2p¾ lines show intense shake-up satellites.
Accession #: 00625-06
Host Material: epitaxial TiN(001) thin film as-deposited
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: 843 s
Total Elapsed Time: 973 s
Number of Scans: 30
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 #:** 00625-07

**Host Material:** epitaxial

TiN(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 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:** 145 s

**Total Elapsed Time:** 274 s

**Number of Scans:** 6

**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.

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### Spectral Features Table

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Peak Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>N 2p Hybridization</td>
</tr>
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<td>2.5</td>
<td>Ti 3d</td>
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<tr>
<td>4.0</td>
<td>E_f</td>
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</tbody>
</table>

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![Graph showing UPS spectrum with peaks labeled Δ₁, Δ₂, Δ₅, and E_f. Peaks are labeled Hybridized N 2p and Ti 3d.]
Accession #: 00625-08
Host Material: epitaxial TiN(001) thin film as-deposited
Technique: UPS
Spectral Region: valence band

Instrument: Physical Electronics, Inc. 5400
Excitation Source: He II
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: 90°
Total Signal Accumulation Time: 1060 s
Total Elapsed Time: 1950 s
Number of Scans: 44
Source Beam Size at Specimen Surface: >5000 μm x >5000 μm
Effective Detector Width: 0.13 eV
Analyzer Width: 1000 μm x 1000 μm unspecified energy
Analyzer Angular Acceptance Width: 14° x 14° at 25 eV
Comment: See footnote below the Spectral Features Table.