Sputter-cleaned Epitaxial $V_{x}Mo_{(1-x)}N_{y}/MgO(001)$ Thin Films Analyzed by X-ray Photoelectron Spectroscopy: 2. Single-crystal $V_{0.47}Mo_{0.53}N_{0.92}$

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Epitaxial $V_{x}Mo_{1-x}N_{y}$ thin films grown by ultrahigh vacuum reactive magnetron sputter deposition on MgO(001) substrates are analyzed by x-ray photoelectron spectroscopy (XPS). This contribution presents analytical results for 300-nm-thick single-crystal $V_{0.47}Mo_{0.53}N_{0.92}/MgO(001)$ films deposited by reactive cosputtering from V (99.95 % purity) and Mo (99.95 % purity) targets. Film growth is carried out in a UHV chamber with base pressure $2 \times 10^{-9}$ Torr at 700 °C in mixed Ar/N$_2$ atmospheres at a total pressure of 5 mTorr, with a N$_2$ partial pressure of 3.2 mTorr; a bias of ~30 V is applied to the substrate. Film composition is determined by Rutherford backscattering spectrometry (RBS). XPS measurements employ monochromatic Al $K_{\alpha}$ radiation ($\hbar \nu = 1486.6$ eV) to analyze $V_{0.47}Mo_{0.53}N_{0.92}(001)$ surfaces sputter-cleaned in-situ with 4 keV Ar$^+$ ions incident at an angle of 70° with respect to the surface normal. XPS results show that the ion-etched sample surfaces have no measurable oxygen or carbon contamination; film composition, obtained using XPS sensitivity factors, is $V_{0.36}Mo_{0.66}N_{0.81}$. All core level peaks, including the nearby Mo 3p$_{3/2}$ and N 1s (at 397.5 eV) peaks, are well-resolved. Comparison to the $V_{0.48}Mo_{0.52}N_{0.64}$ single-crystal film, submitted separately to Surface Science Spectra, indicates that with decreasing growth temperature from 900 to 700 °C (and increasing nitrogen concentration in $V_{x}Mo_{1-x}N_{y}$ from $y = 0.64$ to 0.81) the N 1s core level peak shifts towards lower binding energy by 0.1 eV while all metal atom peaks move in the opposite direction by the same amount.

Keywords: transition metal nitrides; magnetron sputtering; UHV; single crystal; XPS

PACS: 81.15.Cd, 81.15.Dj, 61.50.Lt, 79.60.Dp

INTRODUCTION

$V_{x}Mo_{1-x}N_{y}$ thin film alloys are of interest, not only because, like all transition-metal nitrides they exhibit high hardness, but they have recently been shown to possess unusually high ductility (i.e., high toughness, the resistance to brittle fracture by crack formation and propagation) (Refs. 1 and 2). Here, we use x-ray photoelectron spectroscopy (XPS) to analyze the surface of single crystalline, as determined by a combination of x-ray diffraction and transmission electron microscopy, $V_{0.47}Mo_{0.53}N_{0.92}$ thin films grown by ultrahigh vacuum reactive magnetron sputtering. (See Ref. 3 for comparison measurements of $V_{0.48}Mo_{0.52}N_{0.64}$ single-crystal film.) The films are deposited on MgO(001) substrates at 700 °C in mixed Ar/N$_2$ atmospheres. Film composition is determined by Rutherford backscattering spectrometry (RBS) using a 2 MeV $2He^+$ beam incident at 172° with a backscattering angle of 132°. XPS analyses are carried out with monochromatic Al $K_{\alpha}$ radiation ($\hbar \nu = 1486.6$ eV) at sample surfaces sputter-cleaned in-situ with 4 keV Ar$^+$ ions incident at an angle of 70° with respect to the surface normal. V 2p$_{3/2}$, Mo 3p$_{3/2}$, Mo 3p$_{1/2}$, Mo 3d$_{5/2}$, Mo 3d$_{3/2}$, and N 1s peaks at 512.7, 520.5, 394.1, 411.7, 228.0, 231.3 and 397.5 eV are well-resolved.

SPECIMEN DESCRIPTION (ACCESSION #01262)

Host Material: $V_{0.47}Mo_{0.53}N_{0.92}$ single crystal thin film
Host Material Characteristics: homogeneous; solid; single crystal; conduct; inorganic compound; thin film
Chemical Name: vanadium-molybdenum-nitride
Source: deposited in UHV by reactive magnetron sputtering
Host Composition: vanadium, molybdenum, nitrogen
Form: single-crystal thin film
As Received Condition: as grown
Analyzed Region: not specified
Ex Situ Preparation/Mounting: Epitaxial $V_{x}Mo_{1-x}N_{y}/MgO(001)$ layers are grown by dual-target reactive magnetron sputtering in a stainless-steel UHV system with a base pressure ~2 × 10$^{-9}$ Torr. The 7.6 cm-diameter targets, V (99.95 % purity) and Mo (99.95 % purity), are separately sputter cleaned with shutters...
shifting the other target and the substrate plate, prior to deposition. Single-crystal MgO(001) substrates are ultrasonically cleaned in acetone and 2-propanol for 5 min and degassed in UHV at 900 °C for 45 min before deposition is initiated. Film growth is carried out at 700 °C in mixed Ar (99.999% purity)/N2 (99.999% purity) atmospheres at a total pressure of 5 mTorr, controlled by a capacitance manometer, with a N2 partial pressure of 3.2 mTorr. A 30 V bias is applied to the substrate during growth. For XPS analyses samples are mounted with a pair of copper clamps onto the stainless steel sample holder.

**In Situ Preparation:** Prior to XPS analyses, VxMo1-xNy surfaces are sputter-cleaned with 4 keV Ar+ ions incident at 70° with respect to the surface normal. The ion current density is 12.7 mA/cm² and the beam is rastered over a 2 × 2 mm² area for two minutes, corresponding to the removal of 32 nm on a polycrystalline Ta2O5 reference sample.

**Pre-Analysis Beam Exposure:** not applicable, sample insensitive to X-rays

**Charge Control:** No charge compensation was used during measurements. Prior to ion sputtering the C 1s signal from surface contaminant layer was recorded to be used as the charging reference.

**Temp. During Analysis:** 300 K

**Pressure During Analysis:** <1 × 10⁻⁷ Pa

**INSTRUMENT DESCRIPTION**

**Manufacturer and Model:** Kratos Analytical Axis Ultra DLD

**Analyzer Type:** Other

**Detector:** MCP stack and delay-line detector

**Number of Detector Elements:** 121

**Analyzer Description:** hemispherical analyzer, mean radius: 165 mm

**INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA —**

### Spectrometer

**Analyzer Mode:** constant pass energy

**Throughput (T=Eb):** N=0

**Excitation Source Window:** not specified

**Excitation Source:** Al Kα, monochromatic

**Source Energy:** 1486.6 eV

**Source Strength:** 225 W

**Signal Mode:** multichannel direct

### Geometry

**Incident Angle:** 54°

**Source to Analyzer Angle:** 54°

**Emission Angle:** 0°

**Specimen Azimuthal Angle:** 0°

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

**Analyzer Angular Acceptance Width:** 30° × 30°

**Ion Gun**

**Manufacturer and Model:** Kratos Analytical MiniBeam IV

**Energy:** 4000 eV

**Current:** 12.7 mA/cm²

**Current Measurement Method:** Faraday cup

**Sputtering Species:** Ar⁺

**Spot Size (unrastered):** 200 µm

**Raster Size:** 2000 µm × 2000 µm

**Incident Angle:** 70°

**Polar Angle:** 70°

**Azimuthal Angle:** 180°

**Comment:** equivalent Ta2O5 sputter rate: 16 nm/min; sputtering performed with a differentially pumped ion gun

**DATA ANALYSIS METHOD**

**Energy Scale Correction:** The C 1s line at 284.5 eV assigned to the adventitious carbon present before the sputter-cleaning is used as the reference for the binding energy scale. The position of this line indicates that there is no surface charging.

**Recommended Energy Scale Shift:** 0 eV

**Peak Shape and Background Method:** A Shirley background was used. Core level peaks corresponding to V and Mo were fitted with asymmetric, Lorentzian-based, peak shapes (LF) that use a Cauchy functional form raised to a power and convoluted with a Gaussian. Asymmetry is introduced by varying the value for the power across the maximum of the Cauchy function. For more details see p. 55 in CasaXPS Manual 2.3.15 rev 1.3 (“The Orange Book”). The N 1s peak was fitted with a Gaussian-Lorentzian line shape.

**Quantitation Method:** Quantification is performed with CasaXPS (version 2.3.16) software and based on peak areas from narrow scans compensated for (i) the energy-dependent transmission function of the spectrometer and (ii) the effect of kinetic energy dependent electron mean free path.

Sensitivity factors are supplied by Kratos Analytical Ltd. (library filename: “casaXPS_KratosAxis-F1s.lib” - in this table the sensitivity factor for the F 1s peak is set to 1).

The Kratos sensitivity factors relate to both components of a spin-orbit split doublet. Following the nomenclature used by Kratos, sensitivity factor is only listed with the major component of the two peaks but this is the value used for BOTH components to get proper composition.

**REFERENCES**


### SPECTRAL FEATURES 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>
<th>Peak Assignment</th>
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<tbody>
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<td>01262-02</td>
<td>V 2p</td>
<td>...</td>
<td>...</td>
<td>...</td>
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<td>01262-02</td>
<td>V 2p_{3/2}</td>
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<td>0.83</td>
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<td>V 2p_{1/2}</td>
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<td>1.20</td>
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<tr>
<td>01262-03</td>
<td>Mo 3p</td>
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<td>...</td>
<td>...</td>
<td>1.903</td>
<td>36.6</td>
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<td>01262-03</td>
<td>Mo 3p_{3/2}</td>
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<tr>
<td>01262-03</td>
<td>Mo 3p_{1/2}</td>
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<td>N 1s</td>
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<td>0.96</td>
<td>7070</td>
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<tr>
<td>01262-04*</td>
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\* not used for quantification

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### GUIDE TO FIGURES

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<th>Spectrum (Accession) #</th>
<th>Spectral Region</th>
<th>Voltage Shift*</th>
<th>Multiplier</th>
<th>Baseline</th>
<th>Comment #</th>
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\* Voltage shift of the archived (as-measured) spectrum relative to the printed figure. The figure reflects the recommended energy scale correction due to a calibration correction, sample charging, flood gun, or other phenomenon.
<table>
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<tr>
<th>Accession #</th>
<th>01262–01</th>
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<tbody>
<tr>
<td>Host Material</td>
<td>( V_{0.47}Mo_{0.53}N_{0.92} ) single crystal thin film</td>
</tr>
<tr>
<td>Technique</td>
<td>XPS</td>
</tr>
<tr>
<td>Spectral Region</td>
<td>survey</td>
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<tr>
<td>Instrument</td>
<td>Kratos Analytical Axis Ultra DLD</td>
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<tr>
<td>Excitation Source</td>
<td>Al ( K_{\alpha} ) monochromatic</td>
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<tr>
<td>Source Energy</td>
<td>1486.6 eV</td>
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<td>Source Strength</td>
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<td>Source Size</td>
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<td>Analyzer Type</td>
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<td>Incident Angle</td>
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<tr>
<td>Emission Angle</td>
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<tr>
<td>Analyzer Pass Energy:</td>
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<tr>
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<tr>
<td>Effective Detector Width</td>
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1262-02

Accession #: 01262–02
Host Material: V$_{0.47}$Mo$_{0.53}$N$_{0.92}$
single crystal thin film
Technique: XPS
Spectral Region: V 2p$_{3/2}$; V 2p$_{1/2}$

Instrument: Kratos Analytical Axis Ultra DLD
Excitation Source: Al K$_\alpha$
monochromatic
Source Energy: 1486.6 eV
Source Strength: 225 W
Source Size: not specified
Analyzer Type: hemispherical analyzer, mean radius: 165 mm
Incident Angle: 54°
Emission Angle: 0°
Analyzer Pass Energy: 10 eV
Analyzer Resolution: 0.10 eV
Total Signal Accumulation Time: 1206 s
Total Elapsed Time: 1300 s
Number of Scans: 20
Effective Detector Width: 1 eV

1262-03

Accession #: 01262–03
Host Material: V$_{0.47}$Mo$_{0.53}$N$_{0.92}$
single crystal thin film
Technique: XPS
Spectral Region: Mo 3p$_{3/2}$; Mo 3p$_{1/2}$; N 1s

Instrument: Kratos Analytical Axis Ultra DLD
Excitation Source: Al K$_\alpha$
monochromatic
Source Energy: 1486.6 eV
Source Strength: 225 W
Source Size: not specified
Analyzer Type: hemispherical analyzer, mean radius: 165 mm
Incident Angle: 54°
Emission Angle: 0°
Analyzer Pass Energy: 10 eV
Analyzer Resolution: 0.10 eV
Total Signal Accumulation Time: 2526 s
Total Elapsed Time: 2800 s
Number of Scans: 20
Effective Detector Width: 1 eV
Accession #: 01262–04
Host Material: V_{0.47}Mo_{0.53}N_{0.92} single crystal thin film
Technique: XPS
Spectral Region: Mo 3d_{5/2}; Mo 3d_{3/2}

Instrument: Kratos Analytical Axis Ultra DLD
Excitation Source: Al Kα monochromatic
Source Energy: 1486.6 eV
Source Strength: 225 W
Source Size: not specified
Analyzer Type: hemispherical analyzer, mean radius: 165 mm
Incident Angle: 54°
Emission Angle: 0°
Analyzer Pass Energy: 10 eV
Analyzer Resolution: 0.10 eV
Total Signal Accumulation Time: 966 s
Total Elapsed Time: 1100 s
Number of Scans: 20
Effective Detector Width: 1 eV