Sputter-cleaned Epitaxial $V_xMo_{(1-x)}N_y/MgO(001)$ Thin Films Analyzed by X-ray Photoelectron Spectroscopy: 3. Polycrystalline $V_{0.49}Mo_{0.51}N_{1.02}$

Grzegorz Greczynski^{a)} and Hanna Kindlund
 Linköping University, Department of Physics, Linköping, 581 83, Sweden

Ivan Petrov and Joe Greene
 University of Illinois, Materials Science Department and Frederick Seitz Materials Research Laboratory, Urbana, Illinois, 61801, USA

Lars Hultman
 Linköping University, Department of Physics, Linköping, 581 83, Sweden

(Received 26 June 2013; accepted 16 September 2013; published 8 October 2013)

$V_xMo_{(1-x)}N_y$ 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 002-textured polycrystalline $V_{0.49}Mo_{0.51}N_{1.02}$ films deposited by reactive cosputtering from V (99.95 % purity) and Mo (99.95 % purity) targets. Film growth is carried out at 500 °C in mixed Ar/N₂ atmospheres at a total pressure of 5 mTorr, with a N₂ partial pressure of 3.2 mTorr; a bias of −30 V is applied to the substrate. Films composition is determined by Rutherford backscattering spectrometry (RBS). XPS measurements employ monochromatic Al K_α radiation ($h\nu = 1486.6$ eV) to analyze $V_{0.49}Mo_{0.51}N_{1.02}$ surface 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 $V_{0.34}Mo_{0.66}N_{1.00}$. All core level peaks, including the nearby Mo 3p_{3/2} (binding energy of 394.3 eV) and N 1s (at 397.4 eV) peaks, are well-resolved. Comparison to $V_{0.33}Mo_{0.67}N_{0.64}$ and $V_{0.34}Mo_{0.66}N_{0.81}$ single-crystal film surfaces, submitted separately to *Surface Science Spectra*, indicates that with decreasing growth temperature from 900 to 700 and 500 °C (and increasing nitrogen concentration in $V_xMo_{(1-x)}N_y$ from $y = 0.64$ to 0.81 and 1.00) the N 1s core level peak shifts from 397.6 eV to 397.5 eV to 397.4 eV while metal atom peaks move towards higher binding energy by 0.2–0.4 eV. © 2013 American Vacuum Society. [<http://dx.doi.org/10.1116/11.20130602>]

Keywords: transition metal nitrides; magnetron sputtering; UHV; crystalline films; XPS

PACS: 81.15.Cd, 81.15.Kk, 81.65.Cf, 68.55.aj, 68.55.jm, 81.15.Dj

INTRODUCTION

$V_xMo_{(1-x)}N_y$ 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 highly (002)-oriented polycrystalline, as determined by a combination of x-ray diffraction and transmission electron microscopy, $V_{0.49}Mo_{0.51}N_{1.02}$ thin films grown by ultrahigh vacuum reactive magnetron sputtering. (See Refs. 3 and 4, respectively, for comparison spectra of $V_{0.33}Mo_{0.67}N_{0.64}$ and $V_{0.34}Mo_{0.66}N_{0.81}$ single-crystal films.) The films are deposited on MgO(001) substrates at 500 °C in mixed Ar/N₂ atmospheres. Film composition is determined by Rutherford backscattering spectrometry (RBS) using a 2 MeV 2He⁺ beam incident at 10° with a 172° backscattering angle; the data are analyzed using SIMNRA 6.06 software (Ref. 5). XPS analyses are carried out with monochromatic Al K_α radiation ($h\nu = 1486.6$ 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}, V 2p_{1/2}, Mo 3p_{3/2}, Mo 3p_{1/2}, Mo 3d_{5/2}, Mo 3d_{3/2}, and N 1s peaks at 512.9, 520.6, 394.3, 411.9, 228.2, 231.5 and 397.4 eV are well-resolved.

SPECIMEN DESCRIPTION (ACCESSION #01264)

Host Material: polycrystalline $V_{0.49}Mo_{0.51}N_{1.02}$ thin film

Host Material Characteristics: homogeneous; solid; polycrystalline; conductor; inorganic compound; thin film

Chemical Name: vanadium-molybdenum-nitride

Source: deposited in UHV by reactive magnetron sputtering

Host Composition: vanadiummolybdenumnitrogen

Form: polycrystalline thin film

As Received Condition: as grown

Analyzed Region: not specified

Ex Situ Preparation/Mounting: $V_xMo_{(1-x)}N_y/MgO(001)$ layers are grown by dual-target reactive magnetron sputtering in a stainless-steel UHV system with a base pressure $\sim 2 \times 10^{-9}$

^{a)}Author to whom correspondence should be addressed.

Torr. The 7.6 cm-diameter targets, V (99.95 % purity) and Mo (99.95 % purity), are separately sputter cleaned with shutters shielding 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 500°C in mixed Ar/N₂ 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, V_xMo_(1-x)N_y 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 min, 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 sputter cleaning 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 ($T=E^M$): N=0

Excitation Source Window: not specified

Excitation Source: Al K_α, monochromatic

Source Energy: 1486.6 eV

Source Strength: 225 W

Source Beam Size: 2000 μm × 2000 μm

Signal Mode: multichannel direct

■ Geometry

Incident Angle: 54°

Source to Analyzer Angle: 54°

Emission Angle: 0°

Specimen Azimuthal Angle: 90°

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:

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

1. Davide G. Sangiovanni, Lars Hultman, and Vio Chirita, *Acta Mater.* **59**(5), 2121 (2011).
2. Hanna Kindlund, Davide G. Sangiovanni, L. Martinez-de-Olcoz, Jun Lu, Jens Jensen, Jens Birch, Ivan Petrov, Joe E. Greene, Vio Chirita, and Lars Hultman, *Applied Physics Letters - Materials* (in press) (2013).
3. Grzegorz Greczynski, Hanna Kindlund, Ivan Petrov, Joe E. Greene, and Lars Hultman, *Surf. Sci. Spectra* **20**, 68 (2013).
4. Grzegorz Greczynski, Hanna Kindlund, Ivan Petrov, Joe E. Greene, and Lars Hultman, *Surf. Sci. Spectra* **20**, 74 (2013).
5. M. Meyer, *Proceedings of the 15th International Conference on the Application of Accelerators in Research and Industry*, Vol. 475 (American Institute of Physics Conference Proceeding, 1999), Chap. SIMNRA, a Simulation Program, p. 541.

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
01264-02	V 2p	...	...	...	2.116	16.9	V in $V_{0.34}Mo_{0.66}N_{1.00}$
01264-02	V 2p _{3/2}	512.9	0.89	7019	...	...	V in $V_{0.34}Mo_{0.66}N_{1.00}$
01264-02	V 2p _{1/2}	520.6	1.22	2611	...	...	V in $V_{0.34}Mo_{0.66}N_{1.00}$
01264-03	Mo 3p	...	...	...	1.903	33.0	Mo in $V_{0.34}Mo_{0.66}N_{1.00}$
01264-03	Mo 3p _{3/2}	394.3	2.40	6332	...	...	Mo in $V_{0.34}Mo_{0.66}N_{1.00}$
01264-03	Mo 3p _{1/2}	411.9	2.83	3392	...	...	Mo in $V_{0.34}Mo_{0.66}N_{1.00}$
01264-03	N 1s	397.4	1.02	7174	0.477	50.1	N in $V_{0.34}Mo_{0.66}N_{1.00}$
01264-04 ^a	Mo 3d _{5/2}	228.2	0.74	16525	...	...	Mo in $V_{0.34}Mo_{0.66}N_{1.00}$
01264-04 ^a	Mo 3d _{3/2}	231.5	1.02	9190	...	...	Mo in $V_{0.34}Mo_{0.66}N_{1.00}$

^a not used for quantification

GUIDE TO FIGURES						
Spectrum (Accession) #	Spectral Region	Voltage Shift [*]	Multiplier	Baseline	Comment #	
1264-01	survey	0	1	0		
1264-02	V 2p _{3/2} , V 2p _{1/2}	0	1	0		
1264-03	Mo 3p _{3/2} , Mo 3p _{1/2} , N 1s	0	1	0		
1264-04	Mo 3d _{5/2} , Mo 3d _{3/2}	0	1	0		

^{*} 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.

Accession #	01264-01
Host Material	polycrystalline $V_{0.49}Mo_{0.51}N_{1.02}$ thin film
Technique	XPS
Spectral Region	survey
Instrument	Kratos Analytical Axis Ultra DLD
Excitation Source	Al K_{α} monochromatic
Source Energy	1486.6 eV
Source Strength	225 W
Source Size	2 mm $\times$ 2 mm
Analyzer Type	hemispherical analyzer, mean radius: 165 mm
Incident Angle	54°
Emission Angle	0°
Analyzer Pass Energy:	160 eV
Analyzer Resolution	1.60 eV
Total Signal Accumulation Time	121 s
Total Elapsed Time	150 s
Number of Scans	1
Effective Detector Width	16 eV

■ **Accession #:** 01264-02
 ■ **Host Material:** polycrystalline $V_{0.49}Mo_{0.51}N_{1.02}$ thin film
 ■ **Technique:** XPS
 ■ **Spectral Region:** V $2p_{3/2}$; V $2p_{1/2}$

Instrument: Kratos Analytical Axis Ultra DLD
 Excitation Source: Al K_{α} monochromatic
 Source Energy: 1486.6 eV
 Source Strength: 225 W
 Source Size: 2 mm $\times$ 2 mm
 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

■ **Accession #:** 01264-03
 ■ **Host Material:** polycrystalline $V_{0.49}Mo_{0.51}N_{1.02}$ 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_{α} monochromatic
 Source Energy: 1486.6 eV
 Source Strength: 225 W
 Source Size: 2 mm $\times$ 2 mm
 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 #:** 01264-04
- **Host Material:** polycrystalline $V_{0.49}Mo_{0.51}N_{1.02}$ thin film
- **Technique:** XPS
- **Spectral Region:** Mo $3d_{5/2}$; Mo $3d_{3/2}$

Instrument: Kratos Analytical Axis Ultra DLD

Excitation Source: Al K_{α} monochromatic

Source Energy: 1486.6 eV

Source Strength: 225 W

Source Size: 2 mm $\times$ 2 mm

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