The Si₃N₄/TiN Interface: 1. TiN(001) Grown and Analyzed *In situ* using Angle-resolved X-ray Photoelectron Spectroscopy

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Angle-resolved x-ray photoelectron spectroscopy (AR-XPS) was used to analyze as-deposited epitaxial TiN(001) layers grown *in situ*. The films were grown by ultrahigh vacuum reactive magnetron sputtering onto MgO(001) at 600 °C in mixed 1:1 Ar/N₂ discharges maintained at a total pressure of 0.5 Pa (3.75×10^{-3} Torr). AR-XPS spectra were obtained using incident monochromatic Al K_α radiation at 0.83401 nm. The results show that the TiN(001) surfaces are free of O and C. The Ti 2p photoelectron spectra of clean TiN are characterized by 2p_{3/2} and 2p_{1/2} lines appearing at 454.7 and 460.7 eV, each with corresponding satellite lines which are shifted ~2.6 eV to higher binding energies. © 2012 American Vacuum Society.

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INTRODUCTION

The bulk properties of nanostructured materials (nanocomposites and nanolaminates) are often defined by the physical and electronic structure of internal interfaces which are not well understood. Si₃N₄/TiN nanocomposites (TiN nanocrystals encapsulated in a fully percolated SiN_x tissue phase) are an example of a class of superhard materials that has attracted much attention as a model system. In previously reported work (Ref. 1), a series of different 4-ML-thick overlayers were deposited by ultrahigh vacuum magnetron sputtering onto epitaxial TiN(001) on MgO(001) in order to probe the electronic structure of Si₃N₄/TiN(001), Si/TiN(001), and Ti/TiN(001) bilayer interfaces using angle-resolved x-ray photoelectron spectroscopy. The 4-ML overlayer thickness is similar to reported values for the tissue layer in the Si₃N₄/TiN nanocomposite system and is also electron transparent, allowing us to probe the electronic structure of the interface. It was found that these three overlayer/TiN(001) interfaces have distinctly different bonding characteristics, significantly influencing the structure of the Ti 2p photoelectron spectra.

This contribution presents AR-XPS data from the as-deposited surface of epitaxial TiN(001), which serves as the base layer for the bilayers listed above, deposited *in situ* by ultrahigh vacuum reactive magnetron sputtering onto MgO(001).

SPECIMEN DESCRIPTION (ACCESSION #01240)

Host Material: epitaxial TiN(001) thin film

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 magnetron sputtering

Host Composition: TiN

Form: epitaxial thin film

Structure: B1 NaCl structure

History & Significance: In order to understand the nature of the Si₃N₄/TiN interface, stoichiometric TiN(001) was first deposited by ultrahigh vacuum (UHV) reactive magnetron sputtering onto MgO(001) in a growth chamber attached to an analytical

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chamber containing a photoelectron spectrometer. Angle-resolved x-ray photoelectron spectra were obtained from as-deposited TiN(001) surfaces without air exposure.

As Received Condition: direct vacuum transfer from growth chamber

Analyzed Region: same as host material

Ex Situ Preparation/Mounting: not specified

In Situ Preparation: Epitaxial TiN(001) layers were grown in a multichamber UHV system. The turbomolecular-pumped deposition chamber, with a base pressure of $<1 \times 10^{-7}$ Pa ($<1 \times 10^{-9}$ Torr), was equipped with a dc magnetron and isolated from the analytical chamber during growth. MgO(001) substrates ($5 \times 5 \times 0.5$ mm³) were annealed at $T_s = 800^\circ\text{C}$ for 1 h, a procedure known to produce well-ordered MgO(001) 1×1 surfaces as determined by low-energy electron diffraction analyses (Ref. 2). The target, a 5-cm-diameter water-cooled Ti (99.9999%) disc was sputter cleaned in an Ar/N₂ discharge prior to film deposition. The TiN(001) layers were grown by ultrahigh vacuum reactive magnetron sputter deposition onto MgO(001) substrates at 600°C in mixed 1:1 Ar/N₂ discharges maintained at a total pressure of 0.5 Pa (3.75×10^{-3} Torr). The target power was 100 W with an electrically floating substrate potential of 7V. This procedure is known to produce high quality stoichiometric single-crystalline TiN (Ref. 3).

Pre-Analysis Beam Exposure: less than 2 min; no x-ray effects observed

Charge Control: low energy flood gun/magnetic immersion lens combination; filament current = 1.8 A, charge balance = 2.5 V, filament bias = 1 V

Temp. During Analysis: 300 K

Pressure During Analysis: $<3 \times 10^{-7}$ Pa

INSTRUMENT DESCRIPTION

Manufacturer and Model: Kratos Axis Ultra

Analyzer Type: spherical sector

Detector: channeltron

Number of Detector Elements: 8

INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA

Spectrometer

Analyzer Mode: constant pass energy

Throughput ($T=E^N$): $N=0$

Excitation Source Window: not specified

Excitation Source: Al K_{α} , monochromatic

Source Energy: 1486.6 eV

Source Strength: 225 W

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

Signal Mode: multichannel direct

Geometry

Incident Angle: varies by spectrum

Source to Analyzer Angle: 54°

Emission Angle: varies by spectrum

Specimen Azimuthal Angle: 45°

Acceptance Angle from Analyzer Axis: 0°

Comments: $\Theta_e = 0$ and $\Psi_i = 54.7$, (Accession #s 1240-01 to 05); $\Theta_e = 60$ and $\Psi_i = 5.3$, (Accession #s 1240-06 to 10); $\Theta_e = 75$ and $\Psi_i = 20.3$, (Accession #s 1240-11 to 15)

DATA ANALYSIS METHOD

Energy Scale Correction: The binding energy scale was referenced to the Fermi Level, $E_f = 0$. The position of E_f was estimated by subtracting 1/2 of the full width at half maximum (FWHM) from the position of the maximum of the density-of-states, DOS, between 0-3 eV as determined by peak fitting (DS(0.2,320)SGL(20)).

Recommended Energy Scale Shift: Accession #1240-01, 06 and 11, 0 eV; Accession #s 1240-02 to 05, 2.656 eV; Accession #s 1240-07 to 10, 3.032 eV; Accession #s 1240-12 to 15, 1.965 eV

Peak Shape and Background Method: A Shirley background was used (Ref. 4). Asymmetric modified Gaussian/Lorentzian (product formula) line-shapes (Ref. 5 and 6) were used to fit the Ti 2p and N 1s spectra.

Quantitation Method: Quantification was done using peak areas from CasaXPS (version 2.3.15) region definitions for the entire peak envelope (main peaks and satellites). For simplicity, the peak amplitudes and concentrations are listed with the lowest binding energy line of each of the different elements. Sensitivity factors supplied by Kratos Analytical.

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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
01240-02	O 1s	529.7	2.5	2954.7	0.78	0.96	...
01240-03 ^a	Ti 2p _{3/2}	454.7	0.79	431068.6	2.001	48.63	TiN
01240-03 ^b	Ti 2p _{3/2}	457.5	2.74	...	...	...	TiN
01240-03 ^a	Ti 2p _{1/2}	460.7	1.03	...	...	...	TiN
01240-03 ^b	Ti 2p _{1/2}	463.6	1.37	...	...	...	TiN
01240-04	N 1s	397	0.8	94758.5	0.477	50.4	TiN
01240-04 ^c	N 1s	399.5	2.21	...	...	...	TiN
01240-07	O 1s	529.7	1.23	3301.1	0.78	2.29	...
01240-07	O 1s	531.2	1.38	...	...	...	...
01240-07	O 1s	533.2	1.3	...	...	...	...
01240-08 ^a	Ti 2p _{3/2}	454.8	0.85	168509.5	2.001	45.22	TiN
01240-08 ^b	Ti 2p _{3/2}	457.6	2.55	...	...	...	TiN
01240-08 ^a	Ti 2p _{1/2}	460.8	1.11	...	...	...	TiN
01240-08 ^b	Ti 2p _{1/2}	463.7	1.5	...	...	...	TiN
01240-09	N 1s	397.1	0.95	46050.1	0.477	52.19	TiN
01240-09 ^c	N 1s	399.6	2.18	...	...	...	TiN
01240-12	O 1s	530.3	1.89	3656.4	0.78	4.51	...
01240-12	O 1s	532	2	...	...	...	...
01240-12	O 1s	533.9	2	...	...	...	...
01240-13 ^a	Ti 2p _{3/2}	454.9	0.9	96816.6	2.001	46.6	TiN
01240-13 ^b	Ti 2p _{3/2}	457.6	2.57	...	...	...	TiN
01240-13 ^a	Ti 2p _{1/2}	460.9	1.16	...	...	...	TiN
01240-13 ^b	Ti 2p _{1/2}	463.7	1.5	...	...	...	TiN
01240-14	N 1s	397.1	1.04	24245.9	0.477	48.9	TiN
01240-14 ^c	N 1s	399.6	1.59	...	...	...	TiN

^a screened final-state

^b unscreened final-state, plasmon (Ref. 7)

^c plasmon (Ref. 7)

Comment to Spectral Features Table: Quantification was done using peak areas from CasaXPS (version 2.3.15) region definitions for the entire peak envelope (main peaks and satellites). For simplicity, the peak amplitudes and concentrations are listed with the lowest binding energy line of each of the different elements. Sensitivity factors supplied by Kratos Analytical.

GUIDE TO FIGURES					
Spectrum (Accession) #	Spectral Region	Voltage Shift [*]	Multiplier	Baseline	Comment #
1240-01	survey	0	1.00	1000000	1
1240-02	O 1s	−2.656	1.00	0	1
1240-03	Ti 2p	−2.656	1.00	11000	1
1240-04	N 1s	−2.656	1.00	18000	1
1240-05	valence band	−2.656	1.00	400	1
1240-06	survey	0	3.41	500000	2
1240-07	O 1s	−3.032	1.02	4000	2
1240-08	Ti 2p	−3.032	2.41	5000	2
1240-09	N 1s	−3.032	2.49	8000	2
1240-10	valence band	−3.032	2.41	200	2
1240-11	survey	0	5.74	0	3
1240-12	O 1s	−1.965	1.04	4700	3
1240-13	Ti 2p	−1.965	4.35	0	3
1240-14	N 1s	−1.965	4.87	0	3
1240-15	valence band	−1.965	4.20	0	3

^{*} 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.

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

1. $\Theta_e = 0^\circ$
2. $\Theta_e = 60^\circ$
3. $\Theta_e = 75^\circ$

Accession #	01240-01, 01240-06, 01240-11
Host Material	epitaxial TiN(001) thin film
Technique	XPS
Spectral Region	survey
Instrument	Kratos Axis Ultra
Excitation Source	Al K _α monochromatic
Source Energy	1486.6 eV
Source Strength	225 W
Source Size	2 mm × 2 mm
Analyzer Type	spherical sector
Incident Angle	varies by spectrum
Emission Angle	varies by spectrum
Analyzer Pass Energy:	160 eV
Analyzer Resolution	2.4 eV
Total Signal Accumulation Time	270 s
Total Elapsed Time	#01240-01: 530 s; #01240-06: 530 s; #01240-11: 480 s
Number of Scans	2
Effective Detector Width	33.6 eV
Comment	#01240-01: emission angle = 0°; #01240-06: emission angle = 60°; #01240-11: emission angle = 75°

Accession #	01240-02, 01240-07, 01240-12
Host Material	epitaxial TiN(001) thin film
Technique	XPS
Spectral Region	O 1s
Instrument	Kratos Axis Ultra
Excitation Source	Al K_α monochromatic
Source Energy	1486.6 eV
Source Strength	225 W
Source Size	2 mm $\times$ 2 mm
Analyzer Type	spherical sector
Incident Angle	varies by spectrum
Emission Angle	varies by spectrum
Analyzer Pass Energy:	20 eV
Analyzer Resolution	0.3 eV
Total Signal Accumulation Time	#01240-02: 81 s; #01240-07: 81 s; #01240-12: 122 s
Total Elapsed Time	#01240-02: 223 s; #01240-07: 223 s; #01240-12: 335 s
Number of Scans	#01240-02: 10; #01240-07: 10; #01240-12: 15
Effective Detector Width	4.2 eV
Comment	#01240-02: emission angle = 0° ; #01240-07: emission angle = 60° ; #01240-12: emission angle = 75°

Accession #	01240-03, 01240-08, 01240-13
Host Material	epitaxial TiN(001) thin film
Technique	XPS
Spectral Region	Ti 2p
Instrument	Kratos Axis Ultra
Excitation Source	Al K _α monochromatic
Source Energy	1486.6 eV
Source Strength	225 W
Source Size	2 mm × 2 mm
Analyzer Type	spherical sector
Incident Angle	varies by spectrum
Emission Angle	varies by spectrum
Analyzer Pass Energy:	20 eV
Analyzer Resolution	0.3 eV
Total Signal Accumulation Time	#01240-03: 201 s; #01240-08: 201 s; #01240-13: 302 s
Total Elapsed Time	#01240-03: 555 s; #01240-08: 555 s; #01240-13: 832 s
Number of Scans	#01240-03: 10; #01240-08: 10; #01240-13: 15
Effective Detector Width	4.2 eV
Comment	#01240-03: emission angle = 0°; #01240-08: emission angle = 60°; #01240-13: emission angle = 75°

Accession #	01240-04, 01240-09, 01240-14
Host Material	epitaxial TiN(001) thin film
Technique	XPS
Spectral Region	N 1s
Instrument	Kratos Axis Ultra
Excitation Source	Al K_α monochromatic
Source Energy	1486.6 eV
Source Strength	225 W
Source Size	2 mm $\times$ 2 mm
Analyzer Type	spherical sector
Incident Angle	varies by spectrum
Emission Angle	varies by spectrum
Analyzer Pass Energy:	20 eV
Analyzer Resolution	0.3 eV
Total Signal Accumulation Time	#01240-04: 161 s; #01240-09: 161 s; #01240-14: 242 s
Total Elapsed Time	#01240-04: 444 s; #01240-09: 444 s; #01240-14: 666 s
Number of Scans	#01240-04: 10; #01240-09: 10; #01240-14: 15
Effective Detector Width	4.2 eV
Comment	#01240-04: emission angle = 0° ; #01240-09: emission angle = 60° ; #01240-14: emission angle = 75°

Accession #	01240-05, 01240-10, 01240-15
Host Material	epitaxial TiN(001) thin film
Technique	XPS
Spectral Region	valence band
Instrument	Kratos Axis Ultra
Excitation Source	Al K_α monochromatic
Source Energy	1486.6 eV
Source Strength	225 W
Source Size	2 mm $\times$ 2 mm
Analyzer Type	spherical sector
Incident Angle	varies by spectrum
Emission Angle	varies by spectrum
Analyzer Pass Energy:	20 eV
Analyzer Resolution	0.3 eV
Total Signal Accumulation Time	#01240-05: 181 s; #01240-10: 181 s; #01240-15: 272 s
Total Elapsed Time	#01240-05: 499 s; #01240-10: 499 s; #01240-15: 749 s
Number of Scans	#01240-05: 10; #01240-10: 10; #01240-15: 15
Effective Detector Width	4.2 eV
Comment	#01240-05: emission angle = 0° ; #01240-10: emission angle = 60° ; #01240-15: emission angle = 75°