The Si₃N₄/TiN Interface: 5. TiN/Si₃N₄ 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 TiN/Si₃N₄ bilayers grown by ultrahigh vacuum reactive magnetron sputter deposition onto Si(001), with an electrically floating substrate potential of 7 V, in mixed 1:1 Ar/N₂ discharges maintained at a total pressure of 0.5 Pa (3.75×10^{-3} Torr). The Si₃N₄ layers were deposited at room temperature and the 4-ML thick TiN overlayers were grown at 600 °C. AR-XPS spectra were obtained using incident monochromatic Al K_α x-radiation at 0.83401 nm. TiN/Si₃N₄ Ti 2p spectra reveal an unscreened final-state satellite intensity that lies between that of clean TiN(001) and Si₃N₄/TiN(001). © 2012 American Vacuum Society. [<http://dx.doi.org/10.1116/1.1.20121005>]

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INTRODUCTION

The bulk Si₃N₄ 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 data from TiN, 4-ML thick, deposited at 600 °C onto amorphous Si₃N₄ by ultrahigh vacuum reactive magnetron sputtering on Si(001) with an electrically floating substrate potential of −7 V.

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SPECIMEN DESCRIPTION (ACCESSION #01244)

Host Material: Si₃N₄ Thin Film on Ti(001)

CAS Registry #: 25583-20-4, 12033-89-5

Host Material Characteristics: homogeneous; solid; amorphous; conductor; composite; thin film

Chemical Name: titanium nitride, silicon nitride

Host Composition: TiN/Si₃N₄

Form: thin film

Source: grown *in situ* on Si₃N₄

History & Significance: In order to understand the nature of the Si₃N₄/TiN interface, 4-ML of TiN was deposited at 600 °C onto amorphous Si₃N₄ grown at room temperature on Si(001). Both the TiN and amorphous Si₃N₄ layers were deposited *in situ* by ultrahigh vacuum (UHV) reactive magnetron sputter deposition with an electrically-floating substrate potential of −7 V in a deposition chamber attached to an analytical chamber containing a photoelectron spectrometer. Angle-resolved x-ray photoelectron spectra were obtained from TiN/Si₃N₄ surfaces without air exposure.

As Received Condition: direct vacuum transfer from growth chamber
Analyzed Region: same as host material

Ex Situ Preparation/Mounting: The Si substrate was mechanically mounted to a Mo substrate heater using tungsten wire.

In Situ Preparation: Amorphous TiN and Si₃N₄ layers were grown in a multichamber UHV system equipped with two magnetrons isolated from the analytical chamber of the instrument during growth and separated by a distance of 40 cm to minimize cross contamination. The turbomolecular-pumped growth chamber has a base pressure of $<1 \times 10^{-7}$ Pa ($<1 \times 10^{-9}$ Torr). Si(001) substrates ($5 \times 5 \times 0.5$ mm³) were annealed at T_s = 800 °C for 1 h. The targets, 5-cm-diameter water-cooled Ti (99.9999%) and electronic grade Si (99.9999%) discs were cleaned in an Ar/N₂ discharge prior to film growth. The amorphous Si₃N₄ layers were grown by ultra-high vacuum reactive magnetron sputter deposition onto Si(001) at room temperature in mixed 1:1 Ar/N₂ discharges maintained at a total pressure of 0.5 Pa (3.75×10^{-3} Torr) using a target power of 20 W, a substrate potential of -7 V (floating), a procedure known to produce fully nitrated Si₃N₄ (Refs. 2 and 3). The 4-ML-thick TiN layers were then deposited onto amorphous Si₃N₄ without breaking vacuum, at 600 °C and an electrically floating substrate potential of -7 V. The Ti target was sputtered at 100 W (350 V) in 1:1 Ar/N₂ mixtures maintained at 0.5 Pa (3.75×10^{-3} Torr), a procedure previously shown to provide stoichiometric TiN (Ref. 4).

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: Al K_α (monochromated)

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: varies by spectrum

Source to Analyzer Angle: 54°

Emission Angle: varies by spectrum

Specimen Azimuthal Angle: 45°

Acceptance Angle from Analyzer Axis: 0°

Analyzer Angular Acceptance Width: 40° × 40°

Comments: Θ_e = 0 and Ψ_i = 54.7, (Accession #s 1244-01 to 06); Θ_e = 60 and Ψ_i = 5.3, (Accession #s 1244-07 to 12); Θ_e = 75 and Ψ_i = 20.3, (Accession #s 1244-13 to 18)

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 #s 1244-02 to 06, -1.322 eV; Accession #s 1244-08 to 12, -0.662 eV; Accession #s 1244-14 to 18, -0.95 eV

Peak Shape and Background Method: A Shirley background was used (Ref. 5). Asymmetric modified Gaussian/Lorentzian (product formula) line-shapes (Refs. 6 and 7) and Gaussian/Lorentzian (sum formula) line-shapes (Ref. 7) were used to fit the Ti 2p and N 1s spectra. Gaussian/Lorentzian (product formula) line-shapes (Ref. 7) were used to fit the Si 2p 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
01244-02	O 1s	532.2	1.95	6292.7	0.78	7.14	...
01244-03 ^a	Ti 2p _{3/2}	454.9	1.17	92204.3	2.001	10.45	TiN
01244-03 ^b	Ti 2p _{3/2}	457.7	2.37	...	...	...	TiN
01244-03 ^a	Ti 2p _{1/2}	460.9	1.51	...	...	...	TiN
01244-03 ^b	Ti 2p _{1/2}	463.7	1.26	...	...	...	TiN
01244-04	N 1s	397.8	1.72	91196.1	0.477	44.84	Si ₃ N ₄ /TiN
01244-05	Si 2p _{3/2}	102.2	1.51	35665.1	0.328	37.57	Si ₃ N ₄
01244-05	Si 2p _{1/2}	102.8	1.51	...	...	...	Si ₃ N ₄
01244-08	O 1s	532.1	2.51	4082.2	0.78	8.28	...
01244-09 ^a	Ti 2p _{3/2}	454.9	0.96	69974.4	2.001	14.17	TiN
01244-09 ^b	Ti 2p _{3/2}	457.5	2.74	...	...	...	TiN
01244-09 ^a	Ti 2p _{1/2}	460.9	1.25	...	...	...	TiN
01244-09 ^b	Ti 2p _{1/2}	463.6	1.29	...	...	...	TiN
01244-10	N 1s	397.7	1.73	49815.4	0.477	43.78	Si ₃ N ₄ /TiN
01244-11	Si 2p _{3/2}	99.7	1.68	17936.9	0.328	33.77	...
01244-11	Si 2p _{1/2}	100.3	1.68	...	...	...	...
01244-11	Si 2p _{3/2}	102.2	1.51	...	...	...	Si ₃ N ₄
01244-11	Si 2p _{1/2}	102.8	1.51	...	...	...	Si ₃ N ₄
01244-14	O 1s	531.9	2.57	2815.7	0.78	13.84	...
01244-15 ^a	Ti 2p _{3/2}	454.8	0.97	34098	2.001	16.74	TiN
01244-15 ^b	Ti 2p _{3/2}	457.4	2.78	...	...	...	TiN
01244-15 ^a	Ti 2p _{1/2}	460.8	1.27	...	...	...	TiN
01244-15 ^b	Ti 2p _{1/2}	463.5	1.33	...	...	...	TiN
01244-16	N 1s	397.4	1.77	20060.7	0.477	43.73	Si ₃ N ₄ /TiN
01244-17	Si 2p _{3/2}	102	1.58	5848.4	0.328	26.69	Si ₃ N ₄
01244-17	Si 2p _{1/2}	102.6	1.59	...	...	...	Si ₃ N ₄

^a screened final-state^b unscreened final-state

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 #
1244-01	survey	0	1.00	550000	1
1244-02	O 1s	1.322	1.00	1250	1
1244-03	Ti 2p	1.322	1.00	5500	1
1244-04	N 1s	1.322	1.00	9000	1
1244-05	Si 2p	1.322	1.00	3500	1
1244-06	valence band	1.322	1.00	175	1
1244-07	survey	0	3.55	275000	2
1244-08	O 1s	0.662	1.97	−250	2
1244-09	Ti 2p	0.662	1.25	3000	2
1244-10	N 1s	0.662	1.98	4000	2
1244-11	Si 2p	0.662	2.01	2000	2
1244-12	valence band	0.662	1.76	75	2
1244-13	survey	0	7.34	0	3
1244-14	O 1s	0.95	3.01	0	3
1244-15	Ti 2p	0.95	2.63	0	3
1244-16	N 1s	0.95	4.76	0	3
1244-17	Si 2p	0.95	6.26	0	3
1244-18	valence band	0.95	3.68	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 #	01244-01, 01244-07, 01244-13
Host Material	TiN/Si ₃ N ₄ bilayer
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	240 s
Total Elapsed Time	480 s
Number of Scans	2
Effective Detector Width	33.6 eV
Comment	#01244-01: emission angle = 0°; #01244-07: emission angle = 60°; #01244-13: emission angle = 75°

Accession #	01244-02, 01244-08, 01244-14
Host Material	TiN/Si ₃ N ₄ bilayer
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 × 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	#01244-02: 186 s; #01244-08: 405 s; #01244-14: 405 s
Total Elapsed Time	#01244-02: 512 s; #01244-08: 1114 s; #01244-14: 1114 s
Number of Scans	#01244-02: 23; #01244-08: 50; #01244-14: 50
Effective Detector Width	4.2 eV
Comment	#01244-02: emission angle = 0°; #01244-08: emission angle = 60°; #01244-14: emission angle = 75°

Accession #	01244-03, 01244-09, 01244-15
Host Material	TiN/Si ₃ N ₄ bilayer
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	#01244-03: 462 s; #01244-09: 1005 s; #01244-15: 1005 s
Total Elapsed Time	#01244-03: 1271 s; #01244-09: 2764 s; #01244-15: 2764 s
Number of Scans	#01244-03: 23; #01244-09: 50; #01244-15: 50
Effective Detector Width	4.2 eV
Comment	#01244-03: emission angle = 0°; #01244-09: emission angle = 60°; #01244-15: emission angle = 75°

Accession #	01244-04, 01244-10, 01244-16
Host Material	TiN/Si ₃ N ₄ bilayer
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 × 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	#01244-04: 370 s; #01244-10: 805 s; #01244-16: 805 s
Total Elapsed Time	#01244-04: 1018 s; #01244-10: 2214 s; #01244-16: 2214 s
Number of Scans	#01244-04: 23; #01244-10: 50; #01244-16: 50
Effective Detector Width	4.2 eV
Comment	#01244-04: emission angle = 0°; #01244-10: emission angle = 60°; #01244-16: emission angle = 75°

Accession #	01244-05, 01244-11, 01244-17
Host Material	TiN/Si ₃ N ₄ bilayer
Technique	XPS
Spectral Region	Si 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	#01244-05: 266 s; #01244-11: 605 s; #01244-17: 605 s
Total Elapsed Time	#01244-05: 732 s; #01244-11: 1664 s; #01244-17: 1664 s
Number of Scans	#01244-05: 22; #01244-11: 50; #01244-17: 50
Effective Detector Width	4.2 eV
Comment	#01244-05: emission angle = 0°; #01244-11: emission angle = 60°; #01244-17: emission angle = 75°

Accession #	01244-06, 01244-12, 01244-18
Host Material	TiN/Si ₃ N ₄ bilayer
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 × 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	#01244-06: 398 s; #01244-12: 905 s; #01244-18: 905 s
Total Elapsed Time	#01244-06: 1095 s; #01244-12: 2489 s; #01244-18: 2489 s
Number of Scans	#01244-06: 22; #01244-12: 50; #01244-18: 50
Effective Detector Width	4.2 eV
Comment	#01244-06: emission angle = 0°; #01244-12: emission angle = 60°; #01244-18: emission angle = 75°