The Si₃N₄/TiN Interface: 3. Si₃N₄/TiN(001) Grown with a –150 V Substrate Bias 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 Si₃N₄/TiN(001) bilayers grown by ultrahigh vacuum reactive magnetron sputter deposition onto MgO(001), with a substrate potential of –150 V, in mixed 1:1 Ar/N₂ discharges maintained at a total pressure of 0.5 Pa (3.75×10^{-3} Torr). The TiN(001) films were grown at 600 °C and the 4-ML-thick Si₃N₄ overlayers at room temperature. AR-XPS spectra were obtained using incident monochromatic Al K_α x-radiation at 0.83401 nm. Si₃N₄/TiN(001) Ti 2p spectra reveal enhanced unscreened final-state satellite peaks, compared to Ti 2p spectra obtained from uncapped TiN(001), due to decreased electronic screening induced by Si₃N₄/TiN(001) bilayer interfacial polarization. © 2012 American Vacuum Society. [<http://dx.doi.org/10.1116/1.20121003>]

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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.

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This contribution presents data from Si₃N₄, 4-ML-thick, deposited at room temperature onto epitaxial TiN/MgO(001) by ultrahigh vacuum reactive magnetron sputtering on MgO(001) with a –150 V substrate bias.

SPECIMEN DESCRIPTION (ACCESSION #01242)

Host Material: Si₃N₄ Thin Film on Ti(001) by XPS

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

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

Chemical Name: silicon nitride, titanium nitride

Source: Si₃N₄ grown *in situ* on TiN(001) by ultrahigh vacuum magnetron sputtering

Host Composition: Si₃N₄/TiN

Form: thin film

History & Significance: In order to understand the nature of the Si₃N₄/TiN interface, 4-ML of Si₃N₄ was deposited onto stoichiometric TiN(001) on MgO(001). The amorphous Si₃N₄ layers were deposited at room temperature with a substrate

potential of -150 V onto epitaxial TiN/MgO(001) layers, grown at 600°C with an electrically floating substrate potential of -7 V *in situ*, by ultrahigh vacuum (UHV) reactive magnetron sputtering in a deposition chamber attached to an analytical chamber containing a photoelectron spectrometer. Angle-resolved x-ray photoelectron spectra were obtained from as deposited $\text{Si}_3\text{N}_4/\text{TiN}(001)$ samples without air exposure.

As Received Condition: direct vacuum transfer from growth chamber

Analyzed Region: same as host material

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

In Situ Preparation: Amorphous Si_3N_4 and epitaxial TiN/MgO(001) 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). 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 targets, 5-cm-diameter water-cooled Ti (99.9999%) and electronic grade Si (99.999%) discs were cleaned in an Ar/N_2 discharge prior to film growth. The epitaxial TiN(001) layers were grown by ultrahigh vacuum reactive magnetron sputter deposition onto MgO(001) at 600°C in mixed 1:1 Ar/N_2 discharges maintained at a total pressure of 0.5 Pa (3.75×10^{-3} Torr) using a target power of 100 W, and a substrate potential of -7 V (floating). This procedure produces high-quality stoichiometric single-crystalline TiN (Ref. 3). The 4-ML-thick Si_3N_4 layers were then deposited onto epitaxial TiN(001), without breaking vacuum, at room temperature and a substrate bias of -150 V. The Si target was sputtered at 20 W (350 V) in 1:1 Ar/N_2 mixtures maintained at 0.5 Pa (3.75×10^{-3} Torr), a procedure previously shown to provide fully-nitrided amorphous Si_3N_4 (Refs. 4 and 5).

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

Excitation Source Window: not specified

Excitation Source: Al K_{α} , monochromatic

Source Energy: 1486.6 eV

Source Strength: 225 W

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

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°

Analyzer Angular Acceptance Width: $40^\circ \times 40^\circ$

Comments: $\Theta_e = 0$ and $\Psi_i = 54.7$, (Accession #s 1242-01 to 06); $\Theta_e = 60$ and $\Psi_i = 5.3$, (Accession #s 1242-07 to 12); $\Theta_e = 75$ and $\Psi_i = 20.3$, (Accession #s 1242-13 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: 2.276 (Accession #s 1242-02 to -06), 2.622 (Accession #s 1242-08 to -12), 1.867 (Accession #s 1242-14 to -18)

Peak Shape and Background Method: A Shirley background was used (Ref. 6). Asymmetric modified Gaussian/Lorentzian (product formula) line-shapes (Refs. 7 and 8) and Gaussian/Lorentzian (sum formula) line-shapes (Ref. 8) were used to fit the Ti 2p and N 1s spectra. Gaussian/Lorentzian (product formula) line-shapes (Ref. 8) 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
01242-02	O 1s	532.1	2.74	11842.8	0.78	3.3	...
01242-03 ^a	Ti 2p _{3/2}	454.8	0.85	229168.1	2.001	24.88	TiN
01242-03 ^b	Ti 2p _{3/2}	457.3	2.74	...	...	...	TiN
01242-03 ^a	Ti 2p _{1/2}	460.8	1.1	...	...	...	TiN
01242-03 ^b	Ti 2p _{1/2}	463.4	1.79	...	...	...	TiN
01242-04	N 1s	396	1.1	121371.6	0.477	55.28	TiN/Si ₃ N ₄
01242-04	N 1s	397.1	1.11	...	...	...	TiN/Si ₃ N ₄
01242-05	Si 2p _{3/2}	101.6	1.43	24972.6	0.328	16.54	Si ₃ N ₄
01242-05	Si 2p _{1/2}	102.3	1.43	...	...	...	Si ₃ N ₄
01242-08	O 1s	532.2	2.42	8194.4	0.78	4.77	...
01242-09 ^a	Ti 2p _{3/2}	454.9	0.98	68948.8	2.001	15.65	TiN
01242-09 ^b	Ti 2p _{3/2}	457.4	2.53	...	...	...	TiN
01242-09 ^a	Ti 2p _{1/2}	460.9	1.27	...	...	...	TiN
01242-09 ^b	Ti 2p _{1/2}	463.4	2.53	...	...	...	TiN
01242-10	N 1s	395.9	1.1	58597.9	0.477	55.79	TiN/Si ₃ N ₄
01242-10	N 1s	397.3	1.49	...	...	...	TiN/Si ₃ N ₄
01242-11	Si 2p _{3/2}	101.7	1.43	17179.9	0.328	23.79	Si ₃ N ₄
01242-11	Si 2p _{1/2}	102.3	1.43	...	...	...	Si ₃ N ₄
01242-14	O 1s	532.1	2.53	7002.7	0.78	5.97	...
01242-15 ^a	Ti 2p _{3/2}	454.9	1.03	29829.9	2.001	9.91	TiN
01242-15 ^b	Ti 2p _{3/2}	457.4	2.05	...	...	...	TiN
01242-15 ^a	Ti 2p _{1/2}	460.9	1.34	...	...	...	TiN
01242-15 ^b	Ti 2p _{1/2}	463.4	1.56	...	...	...	TiN
01242-16	N 1s	397.3	1.62	38420.6	0.477	53.57	TiN/Si ₃ N ₄
01242-17	Si 2p _{3/2}	101.8	1.46	15063.6	0.328	30.54	Si ₃ N ₄
01242-17	Si 2p _{1/2}	102.4	1.46	...	...	...	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 #
1242-01	survey	0	1.00	700000	1
1242-02	O 1s	−2.276	1.00	−3000	1
1242-03	Ti 2p	−2.276	1.00	14000	1
1242-04	N 1s	−2.276	1.00	15000	1
1242-05	Si 2p	−2.276	1.00	1600	1
1242-06	valence band	−2.276	1.00	600	1
1242-07	survey	0	3.48	350000	2
1242-08	O 1s	−2.622	1.24	−500	2
1242-09	Ti 2p	−2.622	4.03	6000	2
1242-10	N 1s	−2.622	2.55	8000	2
1242-11	Si 2p	−2.622	1.48	1000	2
1242-12	valence band	−2.622	3.92	200	2
1242-13	survey	0	5.90	0	3
1242-14	O 1s	−1.867	1.43	0	3
1242-15	Ti 2p	−1.867	9.28	0	3
1242-16	N 1s	−1.867	4.12	0	3
1242-17	Si 2p	−1.867	1.69	0	3
1242-18	valence band	−1.867	5.95	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 #	01242-01, 01242-07, 01242-13
Host Material	Si ₃ N ₄ /TiN(001) 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	220 s
Total Elapsed Time	475 s
Number of Scans	2
Effective Detector Width	33.6 eV
Comment	#01242-01: emission angle = 0°; #01242-07: emission angle = 60°; #01242-13: emission angle = 75°

Accession #	01242-02, 01242-08, 01242-14
Host Material	$\text{Si}_3\text{N}_4/\text{TiN}(001)$ 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 $\times$ 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	#01242-02: 82 s; #01242-08: 81 s; #01242-14: 81 s
Total Elapsed Time	#01242-02: 225 s; #01242-08: 223 s; #01242-14: 223 s
Number of Scans	#01242-02: 9; #01242-08: 10; #01242-14: 10
Effective Detector Width	4.2 eV
Comment	#01242-02: emission angle = 0° ; #01242-08: emission angle = 60° ; #01242-14: emission angle = 75°

Accession #	01242-03, 01242-09, 01242-15
Host Material	Si ₃ N ₄ /TiN(001) 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	#01242-03: 199 s; #01242-09: 724 s; #01242-15: 804 s
Total Elapsed Time	#01242-03: 548 s; #01242-09: 1110 s; #01242-15: 2219 s
Number of Scans	#01242-03: 9; #01242-09: 36; #01242-15: 40
Effective Detector Width	4.2 eV
Comment	#01242-03: emission angle = 0°; #01242-09: emission angle = 60°; #01242-15: emission angle = 75°

Accession #	01242-04, 01242-10, 01242-16
Host Material	Si ₃ N ₄ /TiN(001) 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	#01242-04: 145 s; #01242-10: 161 s; #01242-16: 161 s
Total Elapsed Time	#01242-04: 400 s; #01242-10: 444 s; #01242-16: 444 s
Number of Scans	#01242-04: 8; #01242-10: 10; #01242-16: 10
Effective Detector Width	4.2 eV
Comment	#01242-04: emission angle = 0°; #01242-10: emission angle = 60°; #01242-16: emission angle = 75°

Accession #	01242-05, 01242-11, 01242-17
Host Material	Si ₃ N ₄ /TiN(001) 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	#01242-05: 113 s; #01242-11: 121 s; #01242-17: 121 s
Total Elapsed Time	#01242-05: 312 s; #01242-11: 334 s; #01242-17: 334 s
Number of Scans	#01242-05: 8; #01242-11: 10; #01242-17: 10
Effective Detector Width	4.2 eV
Comment	#01242-05: emission angle = 0°; #01242-11: emission angle = 60°; #01242-17: emission angle = 75°

Accession #	01242-06, 01242-12, 01242-18
Host Material	Si ₃ N ₄ /TiN(001) 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	#01242-06: 145 s; #01242-12: 644 s; #01242-18: 644 s
Total Elapsed Time	#01242-06: 400 s; #01242-12: 1778 s; #01242-18: 1778 s
Number of Scans	#01242-06: 8; #01242-12: 36; #01242-18: 40
Effective Detector Width	4.2 eV
Comment	#01242-06: emission angle = 0°; #01242-12: emission angle = 60°; #01242-18: emission angle = 75°