Single Crystalline Oxygen-free Titanium Nitride by XPS

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X-ray photoelectron spectroscopy (XPS) spectra are presented, which are obtained from an oxygen-free single crystalline (sc-) titanium nitride (TiN) sample. The investigated film has been grown on a magnesium oxide (MgO) single crystal with the (001) orientation. Unbalanced Reactive Magnetron Sputter deposition was used to deposit the TiN film in an argon/nitrogen atmosphere at 5×10^{-3} mbar and a temperature of 800 °C. The sample has been transferred *in situ* from the deposition chamber to the XPS device in order to prevent surface oxidation of the sample. Atomic force microscopy (AFM), X-ray diffraction (XRD), Rutherford backscattering (RBS) and angle resolved (AR-) XPS have been used to characterize the sample in detail. This work is dedicated to the XPS characterization of a representative oxygen-free sc-TiN sample. Detailed scans are presented and discussed for the Ti 2p, O 1s, N 1s, Ti 2s, valence band and Ti LMM regions. The spectra contain shake-ups, surface and bulk plasmons, that can be separated and quantified by the presented evaluation procedure. © 2013 American Vacuum Society. [<http://dx.doi.org/10.1116/11.20121107>]

Keywords: titanium nitride; shake-up; satellite; Tougaard background

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INTRODUCTION

Titanium nitride (TiN) is often used as a protective and decorative coating. There is extensive literature available on XPS spectra of pure TiN (Refs. 1–5 and further references therein). The Ti 2p spectrum of TiN contains, besides the well-known two spin-orbit split peaks Ti 2p_{1/2} and Ti 2p_{3/2}, also shake-ups as well as surface and bulk plasmons. The quantification and the interpretation of the shake-ups have been subject of discussion in the aforementioned papers and have only recently been quantified (Ref. 1). In the present contribution XPS data of a pristine oxygen-free sc-TiN sample are shown and a self-consistent data evaluation recommendation is presented.

SPECIMEN DESCRIPTION (ACCESSION #01247)

Host Material: TiN (001)

CAS Registry #: 25583-20-4

Host Material Characteristics: homogeneous; solid; single crystal; conductor; inorganic compound; coating

Chemical Name: titanium nitride

Source: See History and Significance

Host Composition: TiN

Form: TiN (001) deposited at Empa, Dübendorf

Lot #: 1768 (internal experiment #)

Structure: [001]

History / Significance: Titanium nitride is fabricated by unbalanced magnetron sputtering, where a pure titanium target (99.99%) is used to deposit TiN in an argon-nitrogen atmosphere. The Ar gas has a quality of 6.0 and N₂ of 5.0. The crystallinity of TiN has been

checked by recording pole figures using XRD. RBS measurements show an oxygen concentration in the bulk of less than 0.2 at%. AFM results indicate a roughness S_q of approximately 0.5 nm.

As Received Condition: The sample has been studied as deposited and has been transferred *in situ* ($p < 5 \times 10^{-10}$ mbar) from the deposition chamber to the XPS device.

Analyzed Region: not specified

Ex Situ Preparation/Mounting: A Pt-frame has been deposited on a MgO crystal (001). The Pt-frame functions as an electrical contact. Additionally Mo-bands were used to mount the MgO-sample on a Mo-sample holder.

In Situ Preparation: A TiN film has been deposited on top of this setting (MgO crystal with Pt-frame) before transferring the sample *in situ* to the XPS device. No sputter cleaning or annealing has been performed.

Pre-Analysis Beam Exposure: The sample has been exposed to X-rays up to 24 h.

Charge Control: none

Temp. During Analysis: 300 K

Pressure During Analysis: $< 5 \times 10^{-7}$ Pa

INSTRUMENT DESCRIPTION

Manufacturer and Model: Phi-Instrument Quantum 2000

Analyzer Type: spherical sector

Detector: multichannel detector

Number of Detector Elements: 16

INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA —

■ Spectrometer

Analyzer Mode: constant pass energy

Accession #: 01247

Technique: XPS

Host Material: TiN (001)

Instrument: Phi-Instrument Quantum 2000

Major Elements in Spectra: Ti

Minor Elements in Spectra: N, O

Published Spectra: 7

Spectra in Electronic Record: 10

Spectral Category: reference

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

Excitation Source Window: none

Excitation Source: Al K_{α} , monochromatic

Source Energy: 1486.6 eV

Source Strength: 25 W

Source Beam Size: $100 \mu\text{m} \times 100 \mu\text{m}$

Signal Mode: multichannel direct

■ Geometry

Incident Angle: 0 or 1°

Source to Analyzer Angle: 45°

Emission Angle: 45° or 44°

Specimen Azimuthal Angle: 0°

Acceptance Angle from Analyzer Axis: not specified

DATA ANALYSIS METHOD

Energy Scale Correction: To eliminate surface effects (e.g. due to contamination) all binding energies are obtained by using an exponentially decaying fit function that extrapolates angle resolved XPS data to obtain the bulk value for sc-TiN. For a detailed description of the fitting routine it, see Ref. 1. The presented values are binding energies that were measured and extrapolated for four different TiN samples fabricated using the same deposition parameters. Those four samples were prepared and measured independently from each other within a time period of seven months. The presented error is the standard deviation of the interpolated binding energies of these four sc-TiN samples.

Peak Shape and Background Method: All peak shapes are fitted using a least square fitting procedure with a function described by a Gaussian-Lorentzian product (GL(30), for details see Refs. 1 and 6). The background used is a universal-two para-

meter Tougaard (U2T) background, where C has been chosen to be fixed to $C=355.0 \text{ eV}^2$ and B has been allowed to adjust to the limits on the high binding energy side of the selected peak region (for details see Refs. 1 and 6).

Quantitation Method: After the background removal the peak areas have been corrected using the sensitivity factors according to the first principle method (considering Scofield's cross section [Ref. 7], asymmetry function [Ref. 8], transmission function and the inelastic mean free path).

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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
01247-03	Ti 2p _{3/2}	455.0	1.3	~5000	5.7	8.2	Ti-N
01247-03 ^a	Ti 2p _{3/2}	457.2	3.8	~11000	5.7	18.0	Ti-N, shake-up
01247-03	Ti 2p _{1/2}	460.9	1.3	~2600	2.9	8.2	Ti-N
01247-03 ^a	Ti 2p _{1/2}	462.6	3.8	~5700	2.9	18.0	Ti-N, shake-up
01247-03	Ti 2p _{3/2}	467.5	7.3	~3500	5.7	5.8	Ti-N, surface plasmon
01247-03	Ti 2p _{1/2}	474.0	7.3	~1700	2.9	5.4	Ti-N, surface plasmon
01247-03	Ti 2p	481.4	10.5	~4000	8.5	4.4	Ti-N, first bulk plasmon
01247-03	Ti 2p	507.2	10.6	~1300	8.3	1.5	Ti-N, second bulk plasmon
01247-04	N 1s	397.1	1.1	~5000	1.9	25	N-Ti
01247-04 ^b	N 1s	399.5	2.3	~700	1.9	3.4	N-O
01247-05 ^c	O 1s	530.8	2.2	~400	2.8	1.3	O-Ti
01247-05 ^d	O 1s	533.0	2.2	~300	2.8	0.9	O-N

^a To obtain a correct shake-up to main peak ratio the reader is referred to Ref. 1.

^b This peak at 399.49 ± 0.11 eV is assigned to N-O bonds; it cannot be due to a surface or a bulk plasmon. The surface plasmon in TiN has an energy of 12.7 eV (see Ti 2p spectrum), which is about 5 times higher than the difference between the two peaks in N 1s (2.4 eV).

^c Peak energy and FWHM have been obtained by extrapolating the data of more than 200 spectra, for details see Ref. 1.

^d See annotation of O 1s (O-Ti).

ANALYZER CALIBRATION TABLE

Spectrum ID#	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV·cts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
9 ^a	Au 4f _{7/2}	84.0	0.8	...	...	...	...
10 ^a	Ag 3d _{5/2}	368.2	0.7	...	...	...	...
11 ^a	Cu 2p _{3/2}	932.7	1	...	...	...	...

^a The instrument has been calibrated on a regular time basis by measuring the binding energies of Au 4f_{7/2}, Ag 3d_{5/2} and Cu 2p_{3/2} as well as the transmission function.

GUIDE TO FIGURES

Spectrum (Accession) #	Spectral Region	Voltage Shift*	Multiplier	Baseline	Comment #
1247-01	survey	0	1	0	
1247-02	Ti 2p	0	1	0	raw spectrum
1247-02	Ti 2p	0	1	0	fitted spectra
1247-03	N 1s	0	1	0	
1247-04	O 1s	0	1	0	
1247-05	valence band	0	1	0	
1247-06	Ti 2s	0	1	0	
1247-07	Ti LMM	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 #	01247-01
Host Material	TiN (001)
Technique	XPS
Spectral Region	survey
Instrument	Phi-Instrument Quantum 2000
Excitation Source	Al K_{α} monochromatic
Source Energy	1486.6 eV
Source Strength	25 W
Source Size	0.1 mm $\times$ 0.1 mm
Analyzer Type	spherical sector
Incident Angle	0 or 1°
Emission Angle	45 or 44°
Analyzer Pass Energy:	117.4 eV
Analyzer Resolution	0.5 eV
Total Signal Accumulation Time	~1200 s
Total Elapsed Time	~1260 s
Number of Scans	6
Effective Detector Width	16.8 eV
Analyzer Angular Acceptance Width	20° $\times$ 20°

■ Accession #: 01247-02
 ■ Host Material: TiN (001)
 ■ Technique: XPS
 ■ Spectral Region: Ti 2p

Instrument: Phi-Instrument
 Quantum 2000
 Excitation Source: Al K_α
 monochromatic
 Source Energy: 1486.6 eV
 Source Strength: 25 W
 Source Size: 0.1 mm × 0.1 mm
 Analyzer Type: spherical sector
 Incident Angle: 0 or 1°
 Emission Angle: 45 or 44°
 Analyzer Pass Energy: 58.7 eV
 Analyzer Resolution: 0.125 eV
 Total Signal Accumulation Time:
 336 s
 Total Elapsed Time: ~380 s
 Number of Scans: 15
 Effective Detector Width: 8 eV
 Analyzer Angular Acceptance
 Width: 20° × 20°

■ Accession #: 01247-03
 ■ Host Material: TiN (001)
 ■ Technique: XPS
 ■ Spectral Region: N 1s

Instrument: Phi-Instrument Quantum 2000
 Excitation Source: Al K_{α} monochromatic
 Source Energy: 1486.6 eV
 Source Strength: 25 W
 Source Size: 0.1 mm $\times$ 0.1 mm
 Analyzer Type: spherical sector
 Incident Angle: 0 or 1°
 Emission Angle: 45 or 44°
 Analyzer Pass Energy: 58.7 eV
 Analyzer Resolution: 0.125 eV
 Total Signal Accumulation Time: 336 s
 Total Elapsed Time: ~380 s
 Number of Scans: 15
 Effective Detector Width: 8 eV
 Analyzer Angular Acceptance Width: 20° $\times$ 20°

■ Accession #: 01247-04
 ■ Host Material: TiN (001)
 ■ Technique: XPS
 ■ Spectral Region: O 1s

Instrument: Phi-Instrument Quantum 2000
 Excitation Source: Al K_{α} monochromatic
 Source Energy: 1486.6 eV
 Source Strength: 25 W
 Source Size: 0.1 mm $\times$ 0.1 mm
 Analyzer Type: spherical sector
 Incident Angle: 0 or 1°
 Emission Angle: 45 or 44°
 Analyzer Pass Energy: 58.7 eV
 Analyzer Resolution: 0.125 eV
 Total Signal Accumulation Time: 51 s
 Total Elapsed Time: ~90 s
 Number of Scans: 4
 Effective Detector Width: 8 eV
 Analyzer Angular Acceptance Width: 4° $\times$ 4°

■ **Accession #:** 01247-05
 ■ **Host Material:** TiN (001)
 ■ **Technique:** XPS
 ■ **Spectral Region:** valence band

Instrument: Phi-Instrument Quantum 2000
 Excitation Source: Al K_{α} monochromatic
 Source Energy: 1486.6 eV
 Source Strength: 25 W
 Source Size: 0.1 mm $\times$ 0.1 mm
 Analyzer Type: spherical sector
 Incident Angle: 0 or 1°
 Emission Angle: 45 or 44°
 Analyzer Pass Energy: 58.7 eV
 Analyzer Resolution: 0.125 eV
 Total Signal Accumulation Time: not specified
 Total Elapsed Time: not specified
 Number of Scans: 20
 Effective Detector Width: 8 eV
 Analyzer Angular Acceptance Width: 4° $\times$ 4°

■ **Accession #:** 01247-06
 ■ **Host Material:** TiN (001)
 ■ **Technique:** XPS
 ■ **Spectral Region:** Ti 2s

Instrument: Phi-Instrument Quantum 2000
 Excitation Source: Al K_{α} monochromatic
 Source Energy: 1486.6 eV
 Source Strength: 25 W
 Source Size: 0.1 mm $\times$ 0.1 mm
 Analyzer Type: spherical sector
 Incident Angle: 0 or 1°
 Emission Angle: 45 or 44°
 Analyzer Pass Energy: 58.7 eV
 Analyzer Resolution: 0.125 eV
 Total Signal Accumulation Time: 900 s
 Total Elapsed Time: 3600 s
 Number of Scans: 17
 Effective Detector Width: 8 eV
 Analyzer Angular Acceptance Width: 20° $\times$ 20°

■ **Accession #:** 01247-07
■ **Host Material:** TiN (001)
■ **Technique:** XPS
■ **Spectral Region:** Ti LMM

Instrument: Phi-Instrument Quantum 2000

Excitation Source: Al K_{α} monochromatic

Source Energy: 1486.6 eV

Source Strength: 25 W

Source Size: 0.1 mm $\times$ 0.1 mm

Analyzer Type: spherical sector

Incident Angle: 0 or 1°

Emission Angle: 45 or 44°

Analyzer Pass Energy: 58.7 eV

Analyzer Resolution: 0.125 eV

Total Signal Accumulation Time: 900 s

Total Elapsed Time: 3600 s

Number of Scans: 17

Effective Detector Width: 8 eV

Analyzer Angular Acceptance Width: 20° $\times$ 20°