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Al capping layers for nondestructive x-ray photoelectron spectroscopy analyses of transition-metal nitride thin films

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X-ray photoelectron spectroscopy (XPS) compositional analyses of materials that have been air exposed typically require ion etching in order to remove contaminated surface layers. However, the etching step can lead to changes in sample surface and near-surface compositions due to preferential elemental sputter ejection and forward recoil implantation; this is a particular problem for metal/gas compounds and alloys such as nitrides and oxides. Here, the authors use TiN as a model system and compare XPS analysis results from three sets of polycrystalline TiN/Si(001) films deposited by reactive magnetron sputtering in a separate vacuum chamber. The films are either (1) air-exposed for ≤ 10 min prior to insertion into the ultrahigh-vacuum (UHV) XPS system; (2) air-exposed and subject to ion etching, using different ion energies and beam incidence angles, in the XPS chamber prior to analysis; or (3) Al-capped *in-situ* in the deposition system prior to air-exposure and loading into the XPS instrument. The authors show that thin, 1.5–6.0 nm, Al capping layers provide effective barriers to oxidation and contamination of TiN surfaces, thus allowing nondestructive acquisition of high-resolution core-level spectra representative of clean samples, and, hence, correct bonding assignments. The Ti 2p and N 1s satellite features, which are sensitive to ion bombardment, exhibit high intensities comparable to those obtained from single-crystal TiN/MgO(001) films grown and analyzed *in-situ* in a UHV XPS system and there is no indication of Al/TiN interfacial reactions. XPS-determined N/Ti concentrations acquired from Al/TiN samples agree very well with Rutherford backscattering and elastic recoil analysis results while ion-etched air-exposed samples exhibit strong N loss due to preferential resputtering. The intensities and shapes of the Ti 2p and N 1s core level signals from Al/TiN/Si(001) samples do not change following long-term (up to 70 days) exposure to ambient conditions, indicating that the thin Al capping layers provide stable surface passivation without spallation. © 2015 American Vacuum Society. [<http://dx.doi.org/10.1116/1.4916239>]

I. INTRODUCTION

Refractory ceramic transition-metal (TM) nitride thin films grown by physical vapor deposition attract increasing scientific and technological interest due to their unique properties combining high hardness,^{1–4} good high-temperature oxidation resistance,^{5–7} electrical conductivity ranging from metallic to semiconducting,^{8,9} superconductivity,^{9–11} and optical absorption, which can be tuned across the visible spectrum.⁸ Applications include wear-resistant coatings on high-speed cutting tools^{12,13} and engine components,^{14,15}

diffusion barriers in electronic devices,^{16–20} and bioimplant coatings.²¹ NaCl-structure TM nitride thin films also have wide single-phase fields, which support large vacancy concentrations on the anion sublattice, resulting in the case of TiN,²² in N/Ti ratios which range from 0.6 to 1.0,²³ allowing room-temperature resistivity of epitaxial TiN(001) layers to be controllably varied from 13 to 190 $\mu\Omega$ cm (Ref. 24) and the hardness from 20 to 30 GPa (Ref. 4) as N/Ti is decreased from 1.0 to 0.6.

X-ray photoelectron spectroscopy (XPS) is often used to provide not only compositional analyses of TM-nitride-based pseudobinary, ternary, and higher-order thin film alloys developed for specific applications, but also to acquire

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detailed information regarding elemental bonding configurations. TM nitride films are typically grown by magnetron sputter deposition in vacuum systems that do not contain *in-situ* XPS capability; the films are then air-exposed prior to inserting them into a stand-alone XPS system. Ion etching is used to remove oxygen and other adventitious surface contamination prior to analysis. However, the etching process can lead to preferential elemental sputter ejection, recoil implantation, and structural disorder, all of which render quantitative compositional and chemical analyses extremely challenging.²⁵

In order to circumvent these problems, capping layers have been used to protect the sample surface from air exposure during transport to the XPS instrument. For example, Kramer *et al.* passivated surfaces of metastable $(\text{III-IV})_{1-x}(\text{IV}_2)_x$ semiconducting films with As, which was then desorbed *in-situ* prior to XPS analysis.^{26,27} Thin capping layers (≤ 10 nm) were also used to allow direct XPS verification of barrier integrity and check for cap-layer/sample-surface reactions.²⁸

Here, we investigate the effectiveness of metal capping layers for nondestructive high-resolution XPS analyses of ceramic thin films. We use, as a model materials system, polycrystalline 200-nm-thick NaCl-crystal structure TiN layers grown on Si(001) substrates at 400 °C by reactive magnetron sputter deposition in mixed N_2/Ar atmospheres. The cap layer thickness is optimized such that high-quality XPS spectra of the underlying TiN surface can be obtained without significant attenuation. We select Al as the cap layer for the following reasons: (1) the Al native oxide, < 2 nm thick at room temperature, is stable against spallation;⁵ (2) the Al-N heat of formation ($\Delta_f H_{\text{AlN}}^0 = -3.3$ eV/atom) is lower than that of Ti-N ($\Delta_f H_{\text{TiN}}^0 = -3.5$ eV/atom),²⁹ thus minimizing interfacial reactions; (3) and Al core-level peaks do not overlap with the primary Ti and N signals. We show that Al layers with thickness $d_{\text{Al}} = 1.5$ nm form a dense continuous, oxidized barrier that protects the TiN underlayer and allows for acquisition of high-resolution Ti 2p and N 1s core-level spectra, with clear pronounced satellite features,^{30–33} which are in excellent agreement with those obtained from epitaxial TiN layers grown *in-situ* in an XPS system.³⁴ O 1s spectra reveal no evidence for Ti–O bonding. High-resolution Al 2p scans from 1.5-nm-Al/TiN/Si(001) samples indicate that the entire cap layer is oxidized with no Al/TiN interfacial reactions. In addition, XPS-determined N/Ti compositional ratios, obtained based upon Ti 2p and N 1s peak areas, agree very well with the results of Rutherford backscattering spectroscopy (RBS) and time-of-flight elastic recoil detection analyses (ToF-ERDA).

II. EXPERIMENTAL PROCEDURE

Polycrystalline TiN/Si(001) layers, as well as Al cap layers, are grown in a CemeCon CC800/9 magnetron sputtering system. The targets are cast rectangular 8.8×50 cm² Ti and Al plates (99.99% pure). Shutters are used to protect one target while sputter etching the other, immediately prior to film growth, in order to avoid cross-contamination.

Si(001) substrates, 1.5×1 cm², are cleaned sequentially in acetone and isopropyl alcohol and mounted on a rotary substrate table at a distance of six cm from the target. The system is degassed prior to deposition using a two-step heating cycle: 1 h at 500 °C followed by 1 h during which the temperature is slowly decreased to 400 °C, the deposition temperature T_s . TiN layers, 200-nm thick, are grown in mixed Ar/N_2 atmospheres at a total pressure $P_{\text{tot}} = 3$ mTorr (0.4 Pa). Ar and N_2 flow rates are $f_{\text{Ar}} = 350$ cm³/min and $f_{\text{N}_2} = 50$ cm³/min.

The Ti target is operated in high-power pulsed magnetron sputtering mode at an average power of 1300 W, a pulsing frequency of 1000 Hz, and a duty cycle of 20%. A substrate bias voltage $V_s = 60$ V is applied in synchronous with the target pulses.^{35–39} Following TiN deposition, f_{N_2} is set to zero while f_{Ar} is increased to 400 cm³/min to maintain P_{tot} constant; the Al target is sputter-cleaned for 60 s with both target shutters closed, and the TiN/Si(001) samples are rotated in front of the Al target, which is operated at 0.3 kW dc power for cap-layer deposition. Al overlayers are deposited with thicknesses ranging from 1.5 to 25 nm, based upon deposition rate calibrations. For reference, we also deposit 2- μm -thick Al films on TiN/Si(001) samples.

RBS analyses, using a 2.0 MeV $^4\text{He}^+$ probe beam incident at 10° with respect to the surface normal and detected at a 172° scattering angle, as well as ToF-ERDA measurements employing a 36 MeV $^{127}\text{I}^{8+}$ probe beam incident at 67.5° with recoils detected at 45°, show that the TiN films are slightly understoichiometric with $\text{N}/\text{Ti} = 0.96 \pm 0.01$. Film thicknesses determined from cross-sectional scanning electron microscopy analyses in a LEO 1550 instrument are in good agreement with deposition-rate calibrations.

X-ray diffraction θ - 2θ scans and pole figure measurements show that the TiN films are single-phase with the cubic B1 NaCl structure. The layers are polycrystalline with random in-plane orientation and no strong out-of-plane orientation.

XPS spectra are acquired from air-exposed TiN and Al/TiN films in a Kratos Analytical instrument, with a base pressure of 1.1×10^{-9} Torr (1.5×10^{-7} Pa), using monochromatic Al K α radiation ($h\nu = 1486.6$ eV) with the x-ray anode operated at 225 W. The signal is detected orthogonal to the sample surface. The Fermi edge cut-off is set, using sputter-etched clean Ag foil, to an accuracy of better than ± 0.05 eV and the position of the Ag 3d_{5/2} core-level peak is verified to be 368.30 eV.⁴⁰ All core-level (narrow energy range) spectra are acquired with a pass energy $E_{\text{pass}} = 20$ eV. For the Ag 3d_{5/2} reference peak, this results in a full-width at half maximum FWHM peak intensity of 0.55 eV. For survey (wide energy range) scans, $E_{\text{pass}} = 160$ eV resulting in a Ag 3d_{5/2} FWHM of 2.00 eV. Quantification is performed using CASAXPS software (version 2.3.16), based upon peak areas from narrow energy range scans with the Shirley-type background removed.⁴¹ Elemental sensitivity factors, corrected for (1) the energy-dependent transmission function of the spectrometer, and (2) the effect of kinetic-energy-dependent electron mean free paths, are supplied by Kratos Analytical Ltd.⁴²

Al-capped and uncapped TiN/Si(001) films are exposed to air for ≤ 10 min during transport from the deposition chamber to the XPS system where they are analyzed without further processing. A second set of uncapped TiN samples is subjected to sputter-etching in the XPS instrument prior to analysis using an Ar ion beam with (a) an ion energy $E_{\text{Ar}^+} = 0.5$ keV and a beam incidence angle of $\psi = 70^\circ$ relative to the surface normal; (b) $E_{\text{Ar}^+} = 4$ keV with $\psi = 70^\circ$; (c) $E_{\text{Ar}^+} = 4$ keV, $\psi = 45^\circ$; and (d) $E_{\text{Ar}^+} = 4$ keV, $\psi = 0^\circ$. In all cases, XPS spectra are obtained from a 0.3×0.7 mm² area at the center of the sputter-etched region after removal of ~ 10 nm.

Transport of ions in matter (TRIM),⁴³ a Monte Carlo program included in the stopping power and range of ions in matter (SRIM) software package,⁴⁴ is used to estimate primary-ion and recoil projected ranges in TiN due to Ar ion irradiation during sputter etching.

III. RESULTS

A. XPS analyses of Ar⁺-ion-etched air-exposed TiN/Si(001)

Typical Ti 2p and N 1s core-level spectra acquired from sputter-etched uncapped air-exposed TiN surfaces are shown in Figs. 1(a) and 1(b) for the four sets of E_{Ar^+}/ψ etching conditions. The Ti 2p core-level spectra consist of a spin-orbit split doublet with Ti 2p_{3/2} and Ti 2p_{1/2} components at 455.2 and 461.1 eV, respectively. Both Ti 2p peaks exhibit satellite features on the high binding-energy (BE) side, shifted ~ 2.7 eV above the primary peaks, in agreement with previous XPS analyses of polycrystalline TiN layers grown *in-situ* in an XPS system.^{45,46} To facilitate comparison, the intensities of Ti 2p spectra are normalized to those of the highest intensity features (Ti 2p_{3/2} at 455.2 eV, after subtraction of the low-BE background) for each spectrum. The same scale factors are then used to normalize the corresponding N 1s spectra in Fig. 1(b). The relative intensities of the satellite peaks [see inset in Fig. 1(a)] are highest after sputter etching with $E_{\text{Ar}^+} = 0.5$ keV and $\psi = 70^\circ$; they decrease in intensity upon increasing E_{Ar^+} to 4 keV (at $\psi = 70^\circ$); and decrease even further as ψ is lowered to 45° and 0° , while maintaining E_{Ar^+} at 4 keV. The reduction in the satellite feature intensity due to ion etching is accompanied by increasing background levels on the high BE side. The origin of Ti 2p satellite features from TiN_x films with $x > 0.75$ (Ref. 30) is widely discussed in the literature. Two primary interpretations have been proposed including a decrease in the screening probability of the core-hole created during photoionization by Ti 3d electrons,^{30,32,45} and $t_{1g} \rightarrow 2t_{2g}$ intraband transitions between occupied and unoccupied electron states near the Fermi level (shake-up events).^{31,47} The intensity of the Ti 2p satellite features has also been shown to be sensitive to changes induced by Ar ion bombardment (residual point-defect creation, grain refinement, atomic mixing, Ar trapping in interstitial sites, and N loss due to preferential resputtering of lighter elements) as demonstrated by Haasch *et al.*⁴⁸ for epitaxial TiN/MgO(001) films grown *in-situ*, with no air exposure, in an XPS system

Fig. 1. (Color online) (a) XPS Ti 2p and (b) N 1s core-level spectra acquired from sputter-etched uncapped air-exposed polycrystalline TiN/Si(001) surfaces. The etching conditions are $E_{\text{Ar}^+} = 0.5$ keV/ $\psi = 70^\circ$, 4 keV/ 70° , 4 keV/ 45° , and 4 keV/ 0° .

and then ion-etched with a 3 keV Ar ion beam incident at $\psi = 40^\circ$. Thus, the changes in Ti 2p spectra shown in Fig. 1(a) are indicative of ion-irradiation-induced compositional and structural modifications, which increase with increasing Ar⁺ ion penetration depth ξ .

The N 1s core-level peak at 397.4 eV, Fig. 1(b), is also affected by ion irradiation. The peak intensity decreases, accompanied by peak broadening toward the lower BE side, with increasing ion energy E_{Ar^+} and decreasing ion incidence angle ψ . The satellite feature at ~ 400.2 eV has a lower intensity than the Ti 2p satellites [see Fig. 1(a)], but exhibits a similar shift to higher BE with respect to the N 1s peak and decreases in intensity with increasing E_{Ar^+} and decreasing ψ , i.e., increasing ξ . In addition, the XPS-determined N/Ti ratio decreases from 0.74 ± 0.03 with $E_{\text{Ar}^+} = 0.5$ keV and $\psi = 70^\circ$, to 0.72 ± 0.03 , 0.70 ± 0.03 , and 0.68 ± 0.03 with $E_{\text{Ar}^+} = 4$ keV and $\psi = 70^\circ$, 45° , and 0° , indicating preferential N loss, in agreement with previous reports.⁴⁸

The above results clearly illustrate issues associated with XPS analyses following ion etching of air-exposed TiN surfaces. Both Ti 2p and N 1s core-level spectra are sensitive

to increased residual ion-irradiation-induced damage. The effects are least visible for the lowest E_{Ar^+} and highest ψ values used in these experiments. However, even for this case, the uncapped TiN samples exhibit significant preferential N loss due to resputtering.

B. XPS analyses of Al-capped TiN/Si(001)

Figures 2(a)–2(d) are typical SEM plan-view images of Al/TiN/Si(001) samples with Al cap layer thicknesses d_{Al} ranging from 1.5 to 25 nm. The surface of the sample with the thinnest capping layer is relatively featureless and closely resembles that of the uncapped TiN film (not shown). With increasing d_{Al} , the average feature size increases from <10 nm with $d_{\text{Al}} = 1.5$ nm to 20 ± 10 , 45 ± 15 , and 90 ± 20 nm with $d_{\text{Al}} = 6.0$, 13.5, and 25.0 nm.

Figures 3(a)–3(d) are Ti 2p, N 1s, Al 2p, and O 1s core-level spectra acquired from a series of TiN/Si(001) samples, which were either uncapped or capped with Al layers with thicknesses d_{Al} from 1.5 to 25 nm prior to air exposure. Samples used for this set of spectra are analyzed as-received and not Ar^+ -ion etched.

The core level spectra from TiN/Si(001) samples with no Al overlayer exhibit pronounced effects of air exposure; the Ti 2p spectrum in Fig. 3(a) shows that Ti is present in three chemical states: TiN, TiO_xN_y , and Ti-oxide giving rise to Ti $2p_{3/2}$ peaks at 455.2, 456.7, and 458.2 eV, respectively.^{49,50} The corresponding N 1s spectrum [Fig. 3(b)] also contains three peaks: TiN at 397.4 eV,^{50,51} TiO_xN_y at 396.1 eV,⁴⁹ and a low-intensity TiN satellite at ~ 400.2 eV, while the O 1s spectrum [Fig. 3(d)] consists of two peaks at 529.9 and 531.4 eV attributed to oxygen in Ti-oxide and TiO_xN_y bonding configurations, respectively.^{49,50} Thus, the Ti 2p, N 1s, and O 1s spectra are consistent in indicating the presence of Ti-oxide and TiO_xN_y due to air exposure.

In distinct contrast, spectra recorded from TiN films with Al cap layers exhibit no indication of Ti-oxide or

Ti-oxynitride formation. Ti 2p and N 1s core-level signals, Figs. 3(a) and 3(b), resemble those acquired from epitaxial TiN/MgO(001) layers grown *in-situ* in an XPS system, and analyzed with no air-exposure or Ar^+ ion etching.⁴⁸ The O 1s spectrum, Fig. 3(d), consists of only a single peak at 532.0 eV, shifted toward higher BE with respect to the uncapped sample, corresponding to Al–O bonding in Al-oxide. The Al 2p spectra in Fig. 3(c) reveals that the 1.5-nm-thick Al cap layers are fully oxidized with an oxide peak at 75.1 eV and no observable contribution due to metallic Al.⁴⁰

With increasing Al capping layer thickness d_{Al} , the Ti 2p and N 1s peak intensities decrease due to inelastic electron scattering in the overlayer, as discussed further in Sec. IV. There are no detectable Ti 2p or N 1s peak shifts or shape changes. The O 1s peak increases and shifts slightly from 532.0 to 532.4 eV, due to charging in the Al-oxide layer, characteristic of native Al oxide formation as observed for the 2- μm -thick Al reference layer. The Al 2p spectra in Fig. 3(c) exhibit only a single broad peak at 75.1 eV corresponding to native Al oxide.⁵⁰ The Al 2p spectra from samples with $d_{\text{Al}} \geq 6.0$ nm contain, in addition to the Al–O peak, a metallic Al peak at 72.9 eV,⁴⁰ which increases in intensity with increasing Al layer thickness. For samples with $d_{\text{Al}} = 25$ nm, the Al 2p spectra is essentially identical to that acquired from the 2- μm -thick Al reference layer. The metallic peak has a much lower FWHM allowing spin-orbit splitting ($\Delta E = 0.4$ eV) to be resolved with Al $2p_{3/2} = 72.8$ eV and Al $2p_{1/2} = 73.2$ eV. The BE of the Al-oxide peak increases slightly to 75.5 ± 0.1 eV for samples with cap layer thickness $d_{\text{Al}} = 13.5$ and 25.0 nm. There is no evidence of AlN formation, which would lead to a peak at 74.2 eV,³³ in the Al 2p spectra.

The Ti 2p and N 1s spectra in Figs. 4(a) and 4(b), from uncapped TiN/Si(001) samples ion-etched with $E_{\text{Ar}^+} = 0.5$ keV and $\psi = 70^\circ$ (the conditions resulting in the

FIG. 2. SEM plan-view images of polycrystalline Al/TiN/Si(001) films with Al cap layer thicknesses d_{Al} of: (a) 1.5, (b) 6.0, (c) 13.5, and (d) 25.0 nm.

Fig. 3. (Color online) XPS (a) Ti 2p, (b) N 1s, (c) Al 2p, and (d) O 1s core-level spectra acquired from a series of air-exposed polycrystalline TiN/Si(001) films, which were uncapped and capped with Al overlayers of thickness $d_{\text{Al}} = 1.5, 6.0, 13.5,$ and 25.0 nm prior to air exposure. The samples were analyzed as received with no Ar^+ ion etching.

least sample damage) are directly compared with those obtained from air-exposed, but unetched, Al/TiN/Si(001) samples with 1.5 -nm-thick Al cap layers. To facilitate comparison, Ti $2p_{3/2}$ Ti-N bonding peaks at 455.2 eV are normalized in the manner described earlier. The same scaling factors are then used to normalize the corresponding N 1s spectra in order to illustrate differences in XPS-determined N/Ti ratios.

The Ti 2p satellite intensity obtained from the Al-capped sample is higher than for all Ar^+ ion-etched surfaces and comparable to that acquired from epitaxial TiN/MgO(001) films grown *in-situ* in an XPS system with no air exposure.³⁴ The increase in the background intensities on the high-BE sides of the Ti 2p peaks from the capped sample in Fig. 4(a), due to inelastic electron scattering in the Al overlayer, is very small and does not degrade the primary peak signals.

The intensity of the N 1s Ti-N peak obtained from the 1.5 -nm Al/TiN/Si(001) sample, Fig. 4(b), is much higher than that of all uncapped TiN samples, even those subjected to the mildest etching conditions ($E_{\text{Ar}^+} = 0.5$ keV and $\psi = 70^\circ$) for which the XPS-determined N/Ti ratio is 0.74 ± 0.03 . The N/Ti ratio obtained from the Al-capped TiN sample is 0.98 ± 0.03 , in good agreement with RBS and ToF-ERDA results of 0.96 ± 0.01 . The inset in Fig. 4(b) shows normalized N 1s spectra for uncapped TiN/Si(001) samples ion-etched with $E_{\text{Ar}^+} = 0.5$ keV/ $\psi = 70^\circ$ together with air-exposed, but unetched, Al/TiN/Si(001) samples with 1.5 -nm-thick Al cap layers. The shape of the N 1s spectra acquired from TiN samples with Al capping layers is very similar to that of the air-exposed uncapped TiN/Si(001)

film ion etched with $E_{\text{Ar}^+} = 0.5$ keV and $\psi = 70^\circ$, with the higher BE N 1s satellite peak at ~ 400.2 eV clearly resolved. There is an additional low-intensity, low-BE component in the N 1s spectra, Fig. 4(b), obtained from Al/TiN/Si(001) due to organic contamination during air exposure. This assignment is supported by the fact that the intensity of this feature increases with increasing air exposure time.

C. Stability of Al cap layers versus air-exposure time

The stability of Al cap layers as a function of air-exposure time determines the maximum time allowed for sample transfer between deposition and XPS systems. Here, we focus on the thinnest Al cap layer, $d_{\text{Al}} = 1.5$ nm, which provides the least XPS signal attenuation. Al/TiN/Si(001) multilayers are stored in laboratory air, 23°C and 40% relative humidity, for times ranging from 10 to $100\,000$ min. Figures 5(a)–5(e) show C 1s, Al 2p, O 1s, Ti 2p, and N 1s core-level spectra recorded after $t = 10, 100, 1000, 10\,000,$ and $100\,000$ min of air exposure. The most pronounced change with t is observed in C 1s spectra, which contain three peaks centered at $282.1, 285.6,$ and 289.9 eV, corresponding to the chemical bonding states C–Al, C–C, and C=O (and/or O–C=O).^{50,52} The intensities of the two higher-energy peaks increase with storage time indicating continuous accumulation of adventitious carbon on the surface, while the lower-energy peak, due to interactions at the C/Al interface, remains unchanged. The Al 2p spectra exhibits a single Al-oxide peak at 75.1 eV, with no metallic feature, which does not change in intensity or shape as a function of air exposure time, indicating that 1.5 -nm-thick

FIG. 4. (Color online) XPS (a) Ti 2p and (b) N 1s spectra from uncapped air-exposed for ≤ 10 min polycrystalline TiN/Si(001) samples ion-etched with $E_{\text{Ar}^+} = 0.5$ keV and $\psi = 70^\circ$ compared to an air-exposed, but unetched, Al/TiN/Si(001) sample with a 1.5-nm-thick Al cap layer. To facilitate comparison, each Ti 2p spectrum is normalized to the highest intensity peak (Ti 2p_{3/2} peaks at 455.2 eV); the corresponding N 1s spectra are scaled with the same factors. In order to highlight differences in peak shape, normalized N 1s spectra are shown in the inset in (b).

cap layers form a complete stable oxide in ≤ 10 min of air exposure. There is no indication of interfacial Al/TiN interactions, even for the longest storage times. The only observable change in all other core level signals, Figs. 5(c)–5(e), is a small decrease in signal intensity with storage time due to the increased thickness of the carbon contamination layer; there is no evidence in time-dependent O 1s spectra for the formation of Ti oxide or oxynitride.

IV. DISCUSSION

Results shown in Fig. 1(a) for ion-etched uncapped air-exposed polycrystalline TiN/Si(001) layers with no strong preferred orientation indicate that the Ti 2p satellite intensity decreases with increasing ion energy and ion penetration depth ξ . The corresponding set of N 1s spectra in Fig. 1(b) reveals that upon Ar ion bombardment, both the primary and satellite peaks exhibit a decrease in intensity and the primary peak broadens on the low-BE side. The XPS-determined N/Ti ratios for all ion-etched air-exposed samples are significantly lower than the value obtained from RBS and ERDA analyses, even for the mildest set of ion etching conditions ($E_{\text{Ar}^+} = 0.5$ keV and $\psi = 70^\circ$) and

decreases further with increasing ion penetration depth ξ . Similar effects were reported for epitaxial TiN/MgO(001) films grown and ion-etched *in-situ*, with no air exposure, in an XPS system.⁴⁸

The ion penetration depth ξ , which increases with increasing ion energy E_{Ar^+} and decreasing ion incidence angle ψ , is characterized by the effective depth of collision cascade events, which can be estimated from Monte-Carlo based TRIM simulations of ion/surface interactions, and corresponds to the average TiN primary recoil projected range accounting for straggle. For Ti recoils, $\xi_{\text{Ti}} = 1.2$ nm with $E_{\text{Ar}^+} = 0.5$ keV and $\psi = 70^\circ$, and increases to 2.6, 4.0, and 5.3 nm with $E_{\text{Ar}^+} = 4$ keV and $\psi = 70^\circ$, 45° , and 0° . For N recoils, ξ_{N} increases from 0.6 to 2.3, 4.0, and 5.3 nm for the same ion bombardment conditions. These length scales are comparable to typical XPS probing depths, which are controlled by electron inelastic mean free paths λ . The fraction of the XPS signal intensity I_d originating from a surface layer of thickness d is given by $[1 - \exp(-d/\lambda)]$. With $\lambda = 2.2$ nm (for electrons in TiN with energy $E = 1300$ eV) (Ref. 53) and $d \sim \xi_{\text{Ti}}$ (approximate width of ion-altered surface layer), the percentage contribution to the Ti and N core level XPS signal originating from the Ar⁺ ion beam modified surface layer of thickness d is $\sim 40\%$ with $E_{\text{Ar}^+} = 0.5$ keV and $\psi = 70^\circ$, and increases to ~ 70 , ~ 85 , and $\sim 90\%$ with $E_{\text{Ar}^+} = 4$ keV and $\psi = 70^\circ$, 45° , and 0° . Thus, a significant fraction of the XPS signal arises from an ion-irradiation-altered TiN surface layer even for the mildest set of ion etching conditions used in these experiments and increases to essentially the entire sampling depth in the case of etching with $E_{\text{Ar}^+} = 4$ keV/ $\psi = 0^\circ$. A serious ion-irradiation effect is the loss of N due to preferential resputtering. For the mildest ion etch ($E_{\text{Ar}^+} = 0.5$ keV/ $\psi = 70^\circ$), i.e., lowest ξ , the XPS-determined N/Ti ratio is 0.74 ± 0.03 , much lower than the actual value, 0.96 ± 0.01 , obtained from RBS and ERDA. XPS N/Ti ratios decrease further to 0.68 ± 0.03 as E_{Ar^+} is increased to 4 keV and ψ decreased to 0° .

The use of Al capping layers with thicknesses of 1.5–25.0 nm prevents TiN oxidation during sample air exposure as evident from the Ti 2p, N 1s, and O 1s spectra shown in Figs. 3(a), 3(b), and 3(d). Clean TiN spectral features are preserved, in particular, the Ti 2p and N 1s satellite features are intact, unlike the corresponding spectra from ion-etched air-exposed samples (see Fig. 1). There is no evidence in either the Al 2p or N 1s spectra indicating interfacial Al/TiN reactions. This is consistent with TiN having a larger heat of formation ($\Delta_f H_{\text{TiN}}^0 = -3.5$ eV/atom) than AlN ($\Delta_f H_{\text{AlN}}^0 = -3.3$ eV/atom),²⁹ as well as with earlier studies which show that the Al/TiN interface is stable up to 500 °C,^{54–56} i.e., to a significantly higher temperature than used during Al deposition in the present experiments.

TiN oxidation during air exposure is prevented even by the thinnest Al capping layer, $d_{\text{Al}} = 1.5$ nm, indicating that the overlayer is continuous, in agreement with SEM images [see, for example, Fig. 2(a)] showing a smooth surface. The Al 2p core-level signal in Fig. 3(c) reveals that 1.5-nm-thick Al cap layers are completely oxidized, with no evidence of a

FIG. 5. (Color online) XPS (a) C 1s, (b) Al 2p, (c) O 1s, (d) Ti 2p, and (e) N 1s core-level spectra from air-exposed Al/TiN/Si(001) samples for which the Al cap layer thicknesses are $d_{\text{Al}} = 1.5$ nm. The spectra are recorded following $t = 10, 100, 1000, 10\,000$, and $100\,000$ min of air exposure.

metallic Al peak. We estimate the thickness of the native Al oxide layer, based upon the intensity ratio of the Al 2p oxide to metal core level peaks⁵⁷ acquired from the air-exposed 2- μm -thick Al film, to be 2.1 nm. This is in very good agreement with the value, 2.2 nm, we obtain by assuming that the Al and Al_2O_3 layers are fully dense such that $t_{\text{ox}} = t_{\text{Al}}(\rho_{\text{Al}}M_{\text{ox}})/(\rho_{\text{ox}}M_{\text{Al}}N_{\text{Al}})$, in which t is the layer thickness, ρ is density, M is the mass in amu, and $N_{\text{Al}} = 2$ is the number of Al atoms per oxide molecule.

Ti 2p and N 1s peak intensities from Al/TiN/Si(001) samples decrease with increasing Al capping layer thickness d_{Al} , due to inelastic electron scattering in the cap layer. However, the signal does not decay exponentially with increasing d_{Al} , as would be expected in the case of attenuation by a continuous overlayer for which core-level intensity drops as $\sim \exp(-d_{\text{Al}}/\lambda_{\text{Al}})$, in which λ_{Al} is the inelastic mean free path of Ti 2p and N 1s electrons in Al. This can be interpreted with the help of SEM images in Figs. 2(b)–2(d), which reveal significant surface roughness in

samples with $6.0 \leq d_{\text{Al}} \leq 25.0$ nm. Moreover, the roughness increases with increasing cap layer thickness, thus the average near-surface film density decreases. This accounts for the less-than-exponential decrease in Ti 2p and N 1s core-level intensities with d_{Al} .

Ion-etched air-exposed TiN/Si(001) samples suffer from severe N loss resulting from preferential resputtering; the XPS-determined N/Ti values range from 0.74 ± 0.03 for the mildest etching conditions ($E_{\text{Ar}^+} = 0.5$ keV and $\psi = 70^\circ$) and decrease continuously to 0.68 ± 0.03 for the most severe Ar^+ ion etch ($E_{\text{Ar}^+} = 4$ keV and $\psi = 0^\circ$). In contrast, XPS N/Ti ratio obtained from the Al-capped TiN samples is significantly higher, 0.98 ± 0.03 , in very good agreement with RBS and ToF-ERDA results, 0.96 ± 0.01 .

V. CONCLUSIONS

We show that thin metal layers provide effective barriers to sample oxidation and contamination during air exposure and allow subsequent quantitative XPS analyses in which

ion etching is not required. Here, we use polycrystalline TiN/Si(001) thin films as a model system and demonstrate that deposition of 1.5-nm-thick Al layers prior to air exposure allows nondestructive acquisition of high-resolution core-level spectra representative of clean samples, and hence, provide correct bonding assignments. The Ti 2p and N 1s satellite features, which are sensitive to ion bombardment, exhibit high intensities comparable to those obtained from single-crystal TiN/MgO(001) films grown and analyzed *in-situ* in a ultrahigh-vacuum XPS system; line shapes and peak energies are also in excellent agreement. There is no indication of reaction between the Al cap layers and the underlying TiN films, or for the formation of Ti oxide. XPS-determined N/Ti concentrations acquired from Al/TiN/Si(001) samples agree very well with results obtained by Rutherford backscattering and elastic recoil analyses. In contrast, XPS-determined N/Ti ratios of air-exposed uncapped TiN/Si(001) samples subjected to ion etching to remove oxides and adventitious contamination exhibit clear evidence of strong preferential N loss, which increases with increasing Ar ion energy and decreasing incidence angle.

Al 2p core-level spectra from air-exposed Al/TiN/Si(001) samples reveal that 1.5-nm-thick Al cap layers are immediately fully oxidized with no evidence of a metallic Al XPS peak. However, XPS cap layer spectra exhibit increasingly strong metallic Al peaks as d_{Al} is increased from 6 to 25 nm. For all samples, irrespective of d_{Al} , there is no Al 2p or N 1s spectral indication of AlN_x formation. Moreover, the intensities and shapes of the Ti 2p and N 1s core level signals from TiN do not change following long-term (up to 70 days) sample exposure to ambient conditions prior to analysis showing that the thin Al cap layers provide stable surface passivation without spallation.

The metal cap-layer strategy for eliminating ion etching of air-exposed samples prior to quantitative XPS analyses, demonstrated here for TiN/Si(001) thin films with an Al cap, can be applied to other material systems. The primary requirements for the choice of cap layer material are: (1) it should form a dense, continuous, and stable oxide (no spallation), (2) the cap should be thin to avoid significant signal attenuation from the underlying sample, (3) there should be no cap/sample interfacial reaction, and (4) core-level peaks from the cap layer should not overlap with those from the sample.

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