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Venting temperature determines surface chemistry of magnetron sputtered TiN films

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Abstract

Surface properties of refractory ceramic transition metal nitride thin films grown by magnetron sputtering are essential for resistance towards oxidation necessary in all modern applications. Here, typically neglected factors including exposure to residual process gases following the growth and the venting temperature $T_v$, each affecting the surface chemistry, are addressed for the first time. It is demonstrated for the TiN model materials system that $T_v$ has a substantial effect on the composition and thickness-evolution of the reacted surface layer and should therefore be reported. The phenomena are also shown to have impact for the reliable surface characterization by XPS.

Keywords: venting temperature; surface chemistry; magnetron sputtering; titanium dioxide; titanium nitride
Transition metal (TM) nitride-based thin films grown by physical vapor deposition (PVD) are widely used as protective layers on high-speed cutting tools\textsuperscript{1,2} engine parts\textsuperscript{3,4} as well as diffusion barriers in electronics\textsuperscript{5,6,7}. Coating performance does not only depend on the bulk mechanical properties like hardness or elastic modulus, but also on the resistance towards corrosion and/or oxidation during operation in hostile environments, which are to a large extent determined by surface properties. Thus, ambient-coating interactions modifying the surface chemistry are essential for understanding coating performance and failure mechanisms. Numerous studies have been devoted to investigate oxidation mechanisms of TM-based nitrides\textsuperscript{8,9,10}. More recently, the interaction between TiAlN surfaces and residual as well as environmental gas has been studied theoretically\textsuperscript{11} and experimentally\textsuperscript{12}.

Since the ambient-coating interactions define the impurity incorporation during thin film growth\textsuperscript{13,14}, it is reasonable to assume that they also affect the as grown film surfaces during the exposure to residual gases in the vacuum chamber and subsequently throughout the venting sequence and the following storage. Each of these steps affects surface chemistry especially that films are grown at elevated temperatures (400-500 °C) to ensure high adatom surface mobility needed to form dense layers\textsuperscript{15}, which also increases reaction rates. Unfortunately, the effects of or conditions for residual gas exposure, venting strategy, and the long-term storage are not explicitly addressed in the literature.

In this work we seek to change the status quo by pursuing the role of venting temperature $T_v$, a “hidden” experimental variable often not considered and reported, but, as we show here, defining the surface chemistry of the TiN layers. We employ the previously developed Al-cap technique\textsuperscript{16} to separate the effects of residual gas exposure in the high-vacuum (HV) environment during the post-deposition phase from those introduced during the following venting sequence and air exposure. With the help of x-ray photoelectron spectroscopy (XPS) analyses performed on a series of TiN samples as a function of $T_v$ we find that majority
of surface reaction products, including $\text{TiO}_2$, $\text{TiO}_x\text{N}_y$, and $\text{N}_2$ previously detected after prolonged annealing experiments, form shortly after vent, provided that $T_v$ is sufficiently high. This has implications for all sorts of practical studies where the surface composition of TM layers is assumed to be fixed once the same growth protocol is used. We show both, that this is definitely not the case for the TiN model materials system, and that the venting temperature is a key experimental variable. The implications are paramount even for a reliable surface characterization by XPS since (i) the reference core level spectra obtained from “as-received” films exhibit large dependence on $T_v$, and (ii) the ability to obtain clean oxide-free surfaces by \emph{in-situ} sputter etching decreases with increasing venting temperature.

Polycrystalline TiN thin films are grown on Si(001) substrates biased at -60 V by reactive de magnetron sputtering (DCMS) in a CC800/9 CemeCon AG system using rectangular 8.8×50 cm² target and Ar/N₂ gas mixture. The total pressure during deposition is 3 mTorr (0.4 Pa), while the system base pressure $p_b$ before and after the film growth is $2.3 \times 10^{-6}$ Torr (0.3 mPa) and $1.5 \times 10^{-7}$ Torr (0.02 mPa), respectively. The average target power during 25-min-long deposition is 4 kW resulting in film thickness of 1.2 µm. The substrate temperature $T_s$ is 430 °C as determined with the thermocouple placed next to the sample holder.

$\theta$–2$\theta$ x-ray diffraction scans reveal that TiN films are single-phase NaCl-crystal structure with 111 preferred orientation. Rutherford backscattering spectroscopy (RBS) yields $\text{N}/\text{Ti} = 1\pm0.01$, while time-of-flight energy elastic recoil detection analyses (ToF-E ERDA)\textsuperscript{17} give C and O bulk concentrations of 0.4 and 0.2 at%, respectively.

Following TiN film growth, different venting scenarios with N₂ (99.999 % pure) are investigated: (in all cases $T_v$ is measured next to the sample holder and corresponds to the sample temperature): (1) an immediate vent at $T_v = T_s = 430$ °C, (2) vent at $T_v = 330$ °C after 30 min exposure to residual gases, (3) vent at $T_v = 213$ °C after 100 min exposure, and (4) vent at $T_v = 29$ °C after 840 min exposure. Films are subsequently exposed to laboratory air (40 %
RH) for 10 min necessary to transfer them to the load-lock chamber of the ultra-high-vacuum (UHV) XPS system. To quantify the effect of residual gas exposure in HV two additional TiN films are deposited and Al-capped in-situ in the deposition system prior to air-exposure and loading into the XPS instrument. In the first case Al capping is done immediately (< 10 s) after TiN film growth at $T_s = 430 \, ^\circ C$, while the second sample is capped after 840 min exposure to residual gas in HV. This time is necessary for cooling the sample from 430 to 29 °C at $p_b = 1.5 \times 10^{-7} \, \text{Torr (0.02 mPa)}$.

XPS spectra are acquired from TiN and Al/TiN films in a Kratos Analytical instrument, with a base pressure of $1.1 \times 10^{-9} \, \text{Torr (1.5\times10^{-7} Pa)}$, using monochromatic Al Kα radiation ($h\nu = 1486.6 \, \text{eV}$). All spectra are referenced to the adventitious C-C/C-H carbon contamination C 1s peak at 284.5 eV. Spectra deconvolution and quantification is performed using CasaXPS software employing Shirley-type background, Voigt-type line shapes and manufacturer’s sensitivity factors. The exception is the Ti 2p spectra that require asymmetric Voigt-type functions.

We showed recently that 15-Å-thick Al capping layers provide effective barriers to TiN sample oxidation and contamination during air exposure and allow subsequent quantitative XPS analyses in which destructive ion etching is avoided. The Ti 2p and N 1s spectra from Al/TiN samples were identical to those obtained from single-crystal TiN/MgO(001) films grown and analyzed in-situ in a UHV XPS system. XPS-determined N/Ti concentrations acquired from Al/TiN/Si(001) samples were in excellent agreement with RBS and ToF-E ERDA analyses.

Here, we employ the Al-capping technique to separate the effects of exposure to residual gases in the HV environment from those that result from venting at different temperatures. Figures 1(a) and 1(b) show the Ti 2p and N 1s spectra from Al/TiN films capped either immediately after TiN film growth at 430 °C (Ref 1) or following the 840-min-long exposure to residual gases in HV necessary to cool down to $T_v = 29 \, ^\circ C$ for cap deposition (Ref
2). For both samples $T_v = 29 \, ^\circ\text{C}$. There is only a very subtle change in the appearance of the Ti 2p and N 1s core level spectra indicating that prolonged exposure to residual gases has a minor effect on the chemistry of the surface region probed by XPS.\textsuperscript{22}

Figure 1(a-d) shows four sets of Ti 2p, N 1s, O 1s, and C 1s spectra from TiN films as a function of venting temperature, while the XPS-derived surface elemental compositions are summarized in Figure 2. All core-level signals exhibit pronounced changes as a function of $T_v$ indicating large influence of the latter parameter on the surface chemistry. In order to interpret these results in chemical terms all spectra are deconvoluted taking particular care that not only a qualitative, but also a quantitative self-consistency across all core level signals is achieved.\textsuperscript{23} In the next step, using information about the chemical composition of the surface region, the thickness of the reacted layers is estimated from the relative intensities of contributing signals.

The Ti 2p core-level spectra from the Al-capped TiN sample, thus representative of a passivated (native oxide-free) surface (Fig. 1(a)), consist of a spin-orbit split doublet with Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ peaks at 455.3 and 461.2 eV, respectively. Both Ti 2p components 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 \textit{in-situ}.\textsuperscript{24,25} The origin of the satellite peaks is under debate and the primary interpretations are a decrease in the screening probability of the core-hole created during photoionization by Ti 3d electrons,\textsuperscript{24,26,27,28} and $t_{1g} \rightarrow 2t_{2g}$ intraband transitions between occupied and unoccupied electron states near the Fermi level (shake-up events).\textsuperscript{29,30} The N 1s spectra obtained from the Al/TiN sample, Fig. 1(b), consists of a main peak at 397.5 eV and the low-intensity satellite feature at ~400.2 eV.

With increasing $T_v$ two new features appear in the Ti 2p spectra on the expense of the component assigned to TiN bond, which decreases in intensity. We focus on the stronger spin-split component Ti 2p$_{3/2}$. First, with $T_v = 29 \, ^\circ\text{C}$, a new Ti 2p$_{3/2}$ peak appears at 458.5 eV which
is assigned to the TiO₂ formation.³¹,³² This contribution coincides with the TiN satellite peaks and increases in intensity with increasing $T_v$ to completely dominate the Ti 2p spectrum of the $T_v = 430 \degree C$ sample. An additional peak at 456.9 eV, best visible for samples vented at 213 and 330 °C, indicates the formation of TiOₓNᵧ.³³,³⁴ The latter assignment is confirmed by the evolution of the corresponding N 1s spectra, Fig. 1(b), which shows a continuous decrease of the original TiN peak at 397.5 eV with increasing $T_v$, accompanied by a simultaneous increase of the new TiOₓNᵧ feature at lower BE (396.4 eV).³³,³⁴ There is a good correspondence between the relative intensities of the Ti 2p₃/₂ and N 1s components due to oxynitride, which supports peak assignment.³⁵ N 1s spectrum indicates dramatic loss of N in the case of $T_v = 430 \degree C$ sample – with the domination of TiOₓNᵧ component and the presence of a new broad peak at 402.4 eV. The latter feature has been observed previously following 4 h anneal at 450 °C in O₂ atmosphere³⁶ or 1 h anneal at 400 °C in dry air,³⁴ and is attributed to the interstitial molecular nitrogen formed during TiN oxidation according to \(\text{TiN} + \text{O}_2 \rightarrow \text{TiO}_2 + \frac{1}{2}\text{N}_2\). The evolution of the O 1s spectra, Fig. 1(c), is fully consistent with the peak assignments made for Ti 2p and N 1s core-levels. O 1s signal is dominated by a peak at 529.9 eV assigned to TiO₂ [Ref. 32] that increases with increasing $T_v$, in accordance with the corresponding component in the Ti 2p spectra. There is also a low-intensity feature at the higher BE side of the main O 1s peak at ~531.5 eV, which is composed of several smaller contributions from CO, CO₂, and TiNₓOᵧ. C 1s spectra shown in Fig. 1(d) reveals that C is present on the surface in four chemical states: C-C/C-H (284.5 eV), C-O (286.1 eV), O-C=O (289.1 eV), and C-Ti (282.3 eV).³⁷,³⁸ Three first components which dominate the C 1s spectra are associated with the adventitious carbon contamination. TiC is detected in films with $29 \leq T_v \leq 330 \degree C$.

Once the chemical species present in the surface region are identified, the thickness $d$ of the surface layer chemically modified upon air exposure at different $T_v$ can be estimated from the relative signal intensities in the Ti 2p spectra using³⁹,⁴⁰
\[ d = \lambda_B \ln \left( \frac{N_A \lambda_A I_B}{N_B \lambda_B I_A} + 1 \right) \]

in which \( \lambda \) is the inelastic electron mean free path, \( N \) is the volume density of Ti atoms, and \( I \) is the measured XPS peak intensity. Indices \( A \) and \( B \) refer to the original TiN film and the reacted TiO\(_2\)+TiO\(_x\)N\(_y\) surface layer, respectively. The rutile crystal structure is assumed for TiO\(_2\) and TiO\(_x\)N\(_y\) species and for simplicity we use \( \lambda_A = \lambda_B = 18 \) Å for Ti 2p electrons excited with Al K\(_{\alpha}\) x-rays. [Ref. 41]

Figure 3 is the schematic illustration, emerging from the above analyses, of the TiN film surface air-exposed at different \( T_v \). Chemical modification of the native surface is lowest for the \( T_v = 29 \) °C sample. Both TiO\(_2\) and the oxynitride with the stoichiometry TiO\(_{0.3}\)N\(_{0.7}\) are found at the surface, with the domination of the later species (62 % vs. 38 % TiO\(_2\)). The combined thickness of the TiO\(_2\)/TiO\(_{0.3}\)N\(_{0.7}\) surface layer is 11 Å. Angle-resolved XPS indicates that the TiO\(_2\) component is located closer to the surface. The amount of physisorbed adventitious carbon is highest of all samples (see Fig. 2) and dominated by C-C/C-H species, which likely results from the 840-min-long exposure in HV prior to venting. Small amounts of TiC are detected. With increasing \( T_v \) to 213 °C the thickness of the modified layers increases to 16 Å, while the fraction changes to 50% TiO\(_{0.5}\)N and 50% TiO\(_2\). The amount of C contamination is reduced with respect to 29 °C sample predominantly due to the loss of the C-C/C-H component. The \( T_v = 330 \) °C sample possess 20 Å thick reacted layers of equal fraction TiO\(_{0.4}\)N\(_{1.6}\) and TiO\(_2\), while the amount of adventitious C and TiC species is slightly lower than for the TiN film vented at 213 °C. Drastic changes take place once \( T_v \) is increased to 430 °C – the surface layer gets significantly thicker – 48 Å and is predominantly composed of TiO\(_2\) (84%) with a minor oxynitride component TiO\(_{1.2}\)N\(_{0.8}\) (16%). The carbon contamination increases with respect to the 330 °C sample, while the signal from TiC species is not detected.

Clearly, the spatial elemental composition distribution, the phases formed, as well as the reaction layer architecture all strongly depend on the venting temperature. The thickness of the
chemically stable TiO\textsubscript{2} layer increases with $T_v$, and eventually for $T_v \gtrsim 400$ °C dominates the surface. Thus, the commonly used concept of \textit{as-deposited film state} is flawed and the venting temperature has to be reported as it defines the surface chemistry.

These findings have also practical consequences for XPS analyses. In Figure 4 oxygen concentration depth profiles $C_{O(h)}$ obtained from TiN films vented at 29 °C and 430 °C are shown as a function of sputter time. Interestingly, $C_{O(h)}$ profile of the latter sample saturates at ~14 at\%, which is 3× higher concentration than obtained for the TiN film vented at 29 °C. Clearly, a relatively thick TiO\textsubscript{2} layer formed during the high temperature vent prevents effective \textit{in-situ} cleaning presumably due to forward O implantation and re-deposition with negative effects on Ti 2p and N 1s spectra quality (as observed for these samples, but not shown here).

In conclusion, by employing the Al-cap technique for the TiN model materials system we were able to separate the surface chemistry effects of residual gas exposure in the high-vacuum environment during the post-deposition phase from those introduced by the following venting sequence. XPS analyses performed as a function of venting temperature $T_v$ reveal that the majority of surface reaction products, including TiO\textsubscript{2}, TiO\textsubscript{x}N\textsubscript{y}, and N\textsubscript{2} previously detected after prolonged anneal experiments, form shortly after vent, provided $T_v$ is high enough. These results unequivocally demonstrate that $T_v$ defines the surface chemistry of TiN layers and should therefore routinely be recorded and reported together with other processing conditions for such experiments and production. It is reasonable to assume that findings reported here are also relevant for other transition metal nitrides as well as for compounds that form reaction products with gases contained in the atmosphere. The surface characterization by XPS is also affected since the reference core level spectra obtained from as-received films exhibit large dependence on $T_v$. In addition, the ability to obtain clean oxide-free surfaces by \textit{in-situ} sputter etching decreases with increasing venting temperature.
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**Figure Captions**

Fig. 1. XPS (a) Ti 2p, (b) N 1s, (c) O 1s, and (d) C 1s core-level spectra acquired from a series of polycrystalline TiN/Si(001) films as a function of venting temperature. In addition, results for Al/TiN/Si(001) films capped either immediately after the TiN film growth at 430 °C (Ref 1) or following the 840 min-long exposure in high vacuum necessary to cool down to 29 °C for cap deposition (Ref 2), are also shown.

Fig. 2. XPS-derived elemental composition in the surface region of TiN/Si(001) films plotted as a function of venting temperature.

Fig. 3. Schematic representation of the effects of venting temperature on the surface composition of TiN/Si(001) films.

Fig. 4. A comparison of XPS oxygen concentration depth profiles $C_O(h)$ obtained from air-exposed polycrystalline TiN/Si(001) films following the vent at 29 °C or 430 °C.
REFERENCES

19. Kratos Analytical Ltd.: library filename: “casaXPS_KratosAxis-F1s.lib”
21. Under present conditions of $p_b = 1.5 \times 10^{-7}$ Torr the monolayer (ML) formation time is several seconds. Thus, the TiN spectra obtained from REF1 are characteristic of a native TiN surface with ML coverage of adventitious C and O. The interaction between adsorbed species and TiN film is limited to the very first surface layer and should be clearly distinguished from the case of a few nm thick native oxide that forms upon air exposure. REF1 and REF2 core level spectra from TiN are only slightly changed as 90 % of the signal intensity originates from deeper (unaffected) layers. Note also that the product of background pressure and 840 min-long exposure time in HV environment is more than seven orders of magnitude lower than for the 10 min-long air exposure.
22. Quantitative self-consistency implies that the component peaks from different core-level spectra assigned to the same chemical species (e.g. TiO$_2$ components present both in the Ti 2p and O 1s spectra) should yield the area ratio in agreement with the stoichiometry (in this example 1:2).
25. alternative interpretation of the Ti 2p3/2 peak at 456.9 eV as being due to Ti$_2$O$_3$ would require a corresponding peak in the O 1s spectrum at 531.3 eV [Ref. 32] which is not observed.
**Fig. 1**

(a) Ti 2p

(b) N 1s

(c) O 1s

(d) C 1s

Intensity [a.u.]

Binding Energy [eV]
Fig. 4