Autonomously Self-Reporting Hard Coatings: Tracking the Temporal Oxidation Behavior of TiN by In Situ Sheet Resistance Measurements

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1. Introduction

Although there has been tremendous progress in understanding oxidation and the development of new, highly oxidation resistant materials, tracking oxidation remains a grand challenge for many applications, such as cutting tools or gas turbine engines. Measurements of the oxidation kinetics are commonly employed to predict the lifetime of such components. These predictions are relevant for the oxidation conditions utilized in the appraisal of the kinetics data. However, as oxidation conditions vary, the quality of the predictions is adversely affected. Furthermore, processing of the components may also introduce a variability in oxidation behavior. Thus, a significant safety margin has to be utilized to insure safe operation. Consequently, components will be exchanged prior to the actual end of their individual lifetime. Tracking the progress of oxidation in situ during applications would allow for a significantly enhanced individual component lifetime. Furthermore, the overall sustainability of the cutting or energy conversion process would be enhanced as the component lifetime is utilized to a significantly larger extent.

2. Results and Discussions

2.1. Characterization of As-Deposited and Oxidized TiN Coatings

We employ in situ resistance measurements to track oxidation of TiN as a common high temperature coating material with the aim of implementation in application and demonstrate that the sheet resistance fulfills the above-outlined requirements for an autonomous self-reporting property for tracking the oxidation behavior in TiN thin films.

TiN coatings were deposited by reactive physical vapor deposition (PVD) utilizing high power pulsed magnetron sputtering (HPPMS). Pt electrodes were deposited on top of the TiN thin film at the corners of the samples to prevent oxidation of TiN below the electrical contacts and thus maintain a conductive channel to the remaining TiN during oxidation experiments, see schematic in Figure 1. The X-ray diffraction data in Figure 2 indicate that the as-deposited TiN film crystallizes in the osborne phase. Based on energy dispersive X-ray spectroscopy...
(EDX) measurements utilising a time-of-flight elastic recoil detection analysis (TOF-ERDA) standard the chemical composition of the as-deposited TiN thin film was determined to be $49.8 \pm 2.5$ at.% Ti, and $49.7 \pm 2.5$ at.% N with an oxygen concentration of $0.5 \pm 0.4$ at.%. Thus, the TiN thin films are, within the error of the measurement, stoichiometric. The oxygen contamination is expected to be caused by residual gas incorporation during the deposition process.\[13\] In order to reduce modifications of the surface composition by air exposure, the venting temperature was lower than $65^\circ$C.\[14\] The average film thickness of 11 TiN films deposited in one batch measured by scanning electron microscope (SEM) was $0.99 \pm 0.03 \mu m$ where the deviation of $0.03 \mu m$ corresponds to the calculated standard deviation.

After oxidation in air at $600^\circ$C for 4 h the formation of rutile TiO$_2$ is observed in addition to cubic TiN, see Figure 2. After oxidation at $650^\circ$C for 4 h and $700^\circ$C for 1 h 25 min only rutile and no TiN peaks were observed. Scanning transmission electron microscopy (STEM) imaging of an as-deposited TiN thin film depicted in Figure 3a shows, as expected for HPPMS, a dense, fibrous microstructure. After oxidation a porous oxide is formed on top of TiN consisting of globular grains with increasing grain size towards the surface (Figure 3b−d). Whereas no TiN can be detected for the sample oxidized at $700^\circ$C, TiN remains present below the oxide for oxidation at $600$ and $650^\circ$C for 4 h and no significant microstructural changes can be identified by comparison with the as-deposited films. STEM imaging in combination with elemental maps performed on a lamella cut out of the sample oxidized at $600^\circ$C shows the formation of a titanium containing oxide layer on top of a titanium- and nitrogen-rich thin film above the alumina substrate (Figure 1). Thus, these results are in good agreement with observations of TiO$_2$ and TiN by X-ray diffraction. It is evident that a sharp interface between the oxide and nitride forms.

It has to be noted that the Pt layer in the depicted cross-section stems from the preparation procedure of the lamella and is not related to the Pt contacts deposited. For all oxidized samples, the Pt electrodes protected the underlying TiN from oxidation (not shown here). In literature, oxidation of TiN below a 100 nm e-beam evaporated Pt film have been studied at temperatures 550–650°C and a linear significantly reduced oxidation kinetic was found compared to uncovered TiN.\[15\] It is reasonable to assume that the higher Pt film thickness of $0.33 \pm 0.02 \mu m$ in this study further reduced the kinetics of the oxide formation below the Pt electrodes.

2.2. Sheet Resistance as Autonomous Self-Reporting Property

In situ measurements of the sheet resistance were performed throughout all oxidation procedures in order to allow tracking...
of the progress of oxidation. The average resistivity at room temperature of 11 as-deposited samples was measured to be $0.35 \pm 0.01 \, \mu\Omega \cdot m$ (deviation corresponds to the standard deviation), which is in good agreement with resistivities of PVD-deposited TiN films from literature, being predominantly in the range from 0.18 to 0.8 $\mu\Omega \cdot m$.[16–18] For the fine grained TiN thin films in this study, the comparatively high grain boundary density and the presence of oxygen may cause the increase compared to the lowest reported resistivity of 0.18 $\mu\Omega \cdot m$.[16]

Figure 3 shows the obtained sheet resistances for samples oxidized at 600, 650, and 700 °C in air over the oxidation time. In the first minutes after the samples were introduced into the hot furnace, an increase in the sheet resistance was observed due to the metallic-like temperature dependence of the resistivity of TiN.[17] For longer oxidation times, a strong variation in the time dependence of the sheet resistance for the three chosen temperatures was observed. Oxidation at 600 °C induced a slow increase in sheet resistance with time. Annealing in air at 650 °C resulted in a distinct increase in slope after $\approx 2 \, h$ leading to an increased sheet resistance by a factor of $\approx 15$ after 4 $h$ relative to initial resistance at 650 °C. This increase in sheet resistance due to oxidation is even more pronounced for the highest chosen temperatures. Oxidation at 700 °C induced a slow increase in sheet resistance with time. Annealing in air at 650 °C resulted in a distinct increase in slope after $\approx 2 \, h$ leading to an increased sheet resistance by a factor of $\approx 15$ after 4 $h$ relative to initial resistance at 650 °C. This increase in sheet resistance due to oxidation is even more pronounced for the highest chosen oxidation temperature of 700 °C increasing the resistance by a factor in the order of $10^7$ indicating the complete loss of conductive TiN.

Recently, changes in electrical resistance have been correlated to phase changes in Cr$_2$AlC,[19] while pioneering work by Rauh et al.[20] and Case[21] conducted in the 1990s and 1980s showed that electrical resistance measurements are useful to study the initial stage of oxidation of 50–60 nm thick Cu[20] and of 45 nm thick V[22] films. In contrast to these sub-100 nm investigations on metals, results of in situ measured sheet resistances will be employed to track the remaining film thickness of the approx. 1 $\mu$m thick TiN coatings. According to Van der Pauw,[22] the temperature-dependent resistivity $\rho(T)$ can be described by

$$\rho(T) = d \frac{\pi}{\ln(2)} \bar{R} \cdot f (R_1, R_2, \ldots)$$  \hspace{1cm} (1)

where $d$ is the sample thickness, $\bar{R}$ the average measured resistance at different contact arrangements resulting in resistances $R_1$, $R_2$, ..., and $f$ the correction factor. Rutile TiO$_2$ growing on top of the TiN exhibits a resistivity at room temperature of $\approx 10^{12} \, \mu\Omega \cdot m$,[23] being several orders of magnitude higher compared to TiN and is thus expected to be negligible for the measured resistances. For oxidation of Ti-based systems the formation of metastable anatase TiO$_2$ is known to occur.[24] The resistivity of anatase was measured to be in the range of $10^4 \, \mu\Omega \cdot m$.[25] Hence, the approximation that the conductivity during oxidation is dominated by TiN is also valid for the hypothetical case of initial anatase formation. This is in good agreement with the significant increase in sheet resistance observed for oxidation at 700 °C. The remaining TiN thickness was calculated based on Equation (1) with resistance data measured at a certain oxidation temperature and the resistivity of the as-deposited thin film. To obtain the resistivity as a function of annealing temperature $\rho(T)$, an as-deposited TiN thin film was measured in vacuum at a base pressure of $<1 \, mPa$, see Figure 4.

The calculated film thicknesses throughout the oxidation at 600, 650, and 700 °C are given in Figure 3. Initially, the film thickness of the approx. 0.99 $\pm$ 0.03 $\mu$m thick films is overestimated. This is expected to stem from an inaccurate temperature
determination when the sample is introduced into the hot furnace. Due to the high heating rate temperature differences in-between sample and thermocouple may occur due to different heat capacities until thermal equilibrium may be reached. Hence, the temperature at the thermocouple would be larger than at the sample resulting in an overestimation of resistivity and thus the calculated film thicknesses. The measured higher sheet resistances after longer oxidation times result in reduced remaining TiN film thicknesses. After oxidation for 4 h at 600 and 650 °C sheet resistance deduced TiN thicknesses are calculated to be 0.590 and 0.078 µm, respectively. These values are in good agreement with ex situ STEM measured film thicknesses of 0.54 ± 0.01 µm and 0.09 ± 0.01 µm for 600 and 650 °C, respectively, indicated by the diamond shapes in Figure 3. Deviations in-between the in situ and ex situ techniques are 8.3% and 14.2% for 600 and 650 °C, respectively. However, for the sample oxidized at 650 °C the remaining TiN thickness varies significantly within the area analyzed by STEM. Thus, the relatively high deviation of 14.2% may stem from an inhomogeneous remaining TiN thickness within the sample, as the Van der Pauw measurements indicate an average film thickness, whereas the STEM measurements reveal only spatially resolved and hence local film thicknesses. However, both, the resistance as well as the STEM data consistently indicate that the air exposure at 700 °C for 1 h 25 min results in complete oxidation, see Figure 3b. The measured sheet resistance values clearly suggest complete oxidation after 1 h 4 min.

To evaluate the sample variability, five additional samples taken from a single batch, were annealed in air at 650 °C for varying oxidation times (Figure 5). The calculated film thicknesses based on in situ resistance measurements are depicted in Figure 5 and compared to ex situ measured values obtained by STEM. For all samples the remaining TiN layer thicknesses determined by in situ and ex situ measurements differ by 2%–14%. Hence, the ex situ and in situ determined TiN thicknesses are in very good agreement.

It is noteworthy that the sample to sample variation for the thickness after 2 h oxidation at 650 °C determined by ex situ analysis amounts up to 28%, while resistance derived values indicate a variation of up to 38%. Hence, it is evident that the oxidation behavior of TiN thin films from one deposition batch does vary measurably and significantly. This is expected and in line with one of our starting hypothesis namely that coatings and therefore coated components exhibit individual lifetimes. Therefore, to accurately predict the remaining lifetime of components an in situ measurement is necessary. This would allow for an improvement in process control enabling the safe adjustment of the lifetime to the individual limits of components and thus enhance sustainability. However, in order to make autonomously self-reporting coatings suitable for a broad range of applications, the impact of other potentially active degradation mechanisms (in addition to oxidation) on the autonomous self-reporting property need to be investigated, e.g. loss of coating material due to abrasive wear in cutting applications.

3. Conclusions

The oxidation behavior of stoichiometric osbornite TiN coatings deposited by HPPMS was investigated in air. Sheet resistances were measured in situ throughout oxidation. The temperature dependence of the resistivity of the samples was obtained by annealing experiments in vacuum. Subsequently, residual TiN layer thicknesses were derived from in situ sheet resistances. Obtained TiN film thicknesses were in very good agreement with ex situ STEM measured film thicknesses with deviations in-between 2% and 14%. The presented results clearly show that oxidation induced changes in sheet resistance correlate with the progress of the oxidation.
Hence, the sheet resistance was identified as an autonomous self-reporting property of TiN facilitating in situ tracking of the progress of oxidation. It is evident that coatings and therefore coated components exhibit individual lifetimes. The identification of an autonomous self-reporting property enables future predictions of the remaining, individual lifetime of coated components by in situ measurements.

4. Experimental Section

Synthesis of Coatings: TiN coatings were synthesized in an industrial scale deposition chamber (CC800/8, CemeCon AG, Wuerseleen, Germany). A rectangular (500 × 88 × 10 mm³) Ti target was employed in a reactive PVD process. The base pressure at the deposition temperature of 380 °C was below 2 mPa. An Ar/N₂ atmosphere at a total pressure of 425 mPa with an N₂ partial pressure of 55 mPa was used throughout the deposition. 10 × 10 × 0.5 mm³ sapphire substrates were positioned at a target-to-substrate distance of 100 mm at floating potential. A Meleec HPPMS generator (SIPP2000USB-10-500-S) was set to 500 Hz for a duty cycle of 2.5% and a time-averaged power of 1500 W resulting in a peak power density of 0.5 kW cm⁻². The deposition time was 90 min.

In a second step, platinum electrodes were deposited on the corners of the TiN-coated samples in a lab scale system. A 90 mm diameter Pt target was installed at a target-to-substrate distance of 100 mm. The base pressure was below 1 mPa. An Ar atmosphere was set at a pressure of 500 mPa and a direct current PVD process with a power of 100 W was employed. The samples were kept at floating potential and no heating was applied. Areas of 1.5 × 1.5 mm² on each corner of the TiN thin film were coated, while the center of the samples was shielded by a steel cross.

Characterization: The as-deposited samples were oxidized in a vertical tube air furnace at temperatures of 600, 650, and 700 °C for up to 4 h. Throughout the oxidation process, the sheet resistance was measured employing a Van der Pauw setup including a Keithley 2611B System SourceMeter at a current of 5 mA. For this purpose, 4 Pt wires were mechanically pressed on the 4 Pt electrodes deposited on the corners of the TiN samples by ceramic elements. As a reference measurement, one sample was annealed in a high vacuum vertical tube furnace up to 650 °C at a pressure below 1 mPa, while the sheet resistance was measured using the same Van der Pauw setup.

The structural analysis was performed by means of X-ray diffraction in a Bruker AXS D8 Discover equipped with a General Area Detector Diffraction System with a Cu Kα radiation source at a current of 40 mA and a voltage of 40 kV. The primary beam was collimated with a 0.5 mm pinhole. A constant incident angle of 15° was employed. For the analysis of the microstructure and the measurement of film thickness prior and after oxidation STEM was utilized. For this purpose, cross-sectional lamellae were prepared by a standard lift-out method in a Helios NanoLab 660 DualBeam focused ion beam (FIB) system. STEM imaging was performed at an acceleration voltage of 30 kV. Furthermore, a standardless EDX elemental mapping was performed on the prepared lamella with an EDAX Octane Elect Plus at an acceleration voltage of 10 kV. Additionally, as-deposited samples were analyzed in a Hitachi TM4000Plus SEM equipped with a Bruker QUANTAX 75 EDX. A TiN thin film measured by TOF-ERDA was employed as a standard.

Acknowledgements

The authors kindly acknowledge funding through the Max Planck Fellow Program.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

coatings, oxidation, self-reporting, TiN

Received: January 5, 2020
Published online: February 12, 2020

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