Frictional behaviour of TiN coatings grown by atomic layer deposition

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Abstract. The main idea of the presented work is the evaluation of frictional properties of the TiN coatings deposited by atomic layer deposition technology using atomic force microscopy approach. Ogletree method was employed in order to calibrate the lateral force and estimate the average friction coefficient of TiN coatings. Obtained titanium nitride coatings were also characterized in terms of morphology, surface topography and mechanical properties. The evaluation has been done with reference to the commercially available TiN produced by commonly known magnetron sputtering method.

1. Introduction

Nowadays, material scientists are focused on manufacturing and testing advanced materials (i.e. composites) with excellent and various properties (i.e. high temperature resistance, electrical conductivity). One of the most important property is a resistance to mechanical factors (i.e. friction, fatigue, torsion). Ceramics (i.e. titanium nitride) are known as materials with the best mechanical resistance. Such materials can be used in the space industry, biomedical engineering and wherever structures are exposed to strong mechanical impact. They have also wide application in the production of coatings.

Atomic Layer Deposition (ALD) is a thin-film deposition technique with atomic scale precision growth. During the ALD process occurs saturated chemisorption of gases (precursors) on the surface of substrates. A monoatomic layer is formed in one ALD cycle deposited material. The thickness of the layer depends on the number of deposition cycles. The resulting layers are stoichiometric and show excellent homogeneity over the entire surface.

There are several factors responsible for the differences in friction properties in the micro- and nanoscale. These may include particles that are products of wear and impurities, the transition from elastic to plastic deformation regime as well as the effect of the meniscus formation. One of the extension of atomic force microscopy, enabling measurement of normal and friction forces with pico-Newton resolution is so-called lateral force microscopy (LFM). This technique allows study the tribological properties, including coefficient of friction and wear in the nanometre scale. In this method cantilever with a tip moves on a sample's surface in the vertical direction which causes a torsion of the cantilever.

Titanium nitride is the one of the hardest ceramics material. TiN is often used as a coating on titanium alloys, steel, carbide and aluminium. It is extremely durable, thermally stable and has a very high level of a resistant to chemical etching. TiN has a very high hardness and modulus of elasticity. This material has also outstanding optical properties, it perfectly reflects infrared radiation.
material has a wide application due to these properties. Titanium Nitride is an example of advanced material which can be used in space industry and biomedical engineering. TiN can be used in fuselages of spacecraft and can play a role as a protection against damages and scratching in implants. Additionally, it becomes superconducting at very low temperatures.

2. Materials and methods
2.1. Preparation of coatings
The coatings were synthesized using atomic layer deposition technique. Two different precursors combinations were used for TiN synthesis: i) titanium tetrachloride, TiCl₄ and monomethylhydrazine, MMH (later in this work abbreviated as TiCl₄/MMH) or ii) TiCl₄ and dimethylhydrazine DMH (abbreviated as TiCl₄/DMH). As a substrate material a native oxide silicon wafer was used. For the purpose of achieving higher deposition rates the ALD semi-industrial machine, the Beneq TFS 200 was used. Electron diffraction (EDX) analysis revealed that compositions of obtained TiN films were close to stoichiometry: Ti (40–45.5 at.%) and N (43.5–49 at.%) with low Cl contamination (0.5–1 at.%). Two groups of samples with different thickness (resulted from different number of ALD deposition cycles) and grown at varying temperatures have been selected for further investigation, according to Table 1.

| Sample               | Growth temperature, °C | Number of deposition cycles | Pulses duration, s | Thickness, nm |
|----------------------|-------------------------|-----------------------------|--------------------|---------------|
| TiCl₄/MMH@300°C      | 300°C                   |                             |                    |               |
| TiCl₄/MMH@400°C      | 400°C                   |                             |                    |               |
| TiCl₄/MMH@500°C      | 500°C                   |                             |                    |               |
| TiCl₄/DMH@350°C      | 350°C                   | 600                         | 0.3                | 10-30         |
| TiCl₄/DMH@400°C      | 400°C                   |                             |                    |               |
| TiCl₄/DMH@450°C      | 450°C                   |                             |                    |               |
| TiCl₄/DMH@500°C      | 500°C                   |                             |                    |               |
| TiCl₄/MMH@420°C      | 420°C                   | 7000                        | 0.3                | 80            |

Thickness measurements were performed using X-ray reflectometry (XRR) technique and by depth profiling on nanoindenter. As a reference sample 80 nm thick commercial TiN layer synthesized by magnetron sputtering technique (MS) was used.

2.2. Characterization
Surface morphology, topography and lateral force measurements were performed under ambient conditions using Multimode 5 atomic force microscope equipped with Nanoscope V controller (Bruker Corporation). Topography measurements were made in tapping mode and the size of the images were 1×1 μm. Commercial silicon cantilevers type HQ:NSC15 (MicroMasch) with nominal tip radius ~8 nm, cantilever spring constant of 40 N/m and resonant frequency of 325 kHz were used. Image acquisition was performed with use of Nanoscope 7.3 software and further image processing was done using Nanoscope Analysis 1.9 (Bruker Corporation) and MountainsMap Premium 5.0 (Digital Surf) software.

For friction measurements the areas of 200×200 nm were used at increasing loads up to ~80 nN (10 normal loads ramping equally over the single image) at 1 Hz scan rate according to the procedure described already in our previous papers [1,2]. Commercial silicon cantilevers type HQ:CSC37 (MicroMasch) with nominal tip radius of 8 nm and nominal cantilever spring constant of 0.8 N/m was used. A commercial TGG1 silicon calibration grid (NT-MDT) with 1-D array of triangular steps was used for lateral force calibration [3]. All LFM tests were conducted above adhesion-only regime.
Mechanical properties, hardness and elastic modulus, of the coatings were measured using nanoindentation technique on Nano Indenter G200 system (KLA Corporation). For nanoindentation a diamond Berkovich tip (Micro Star Technologies) and the continuous stiffness measurement mode were used. The tip shape was calibrated by conducting experiments on a fused silica standard and data were analysed using the Oliver and Pharr [4] approach. Nine experiments were performed on each sample at a strain rate of 0.05 s$^{-1}$.

Nano-wear tests were conducted in reciprocating sliding mode with the use of the nanoindenter equipped with a diamond conical tip with 1 µm radius and apex angle of 90 deg. The tests were carried out at low normal force of 6 mN for 100 cycles, sliding distance and frequency of 50 µm and 1 Hz, respectively. All of the tests were performed under ambient conditions. Five experiments under same conditions were performed on each sample. Cross profile measurements in the location of the wear tests allowed wear coefficient calculation, based on Archard equation [5].

3. Results and discussion

3.1. Surface topography

In Fig. 1 AFM surface topography scans of all investigated coatings are presented while the roughness parameters are gathered in Fig. 2. Commonly known geometric surface structure parameters of the samples, average roughness (Ra) and root-mean square roughness (RMS), were defined as average values taken from 512 surface profiles. The error was calculated as the standard deviation among all surface profiles.

In the case of TiN coatings produced in the presence of TiCl$_4$/MMH precursors a clear proportional relationship between the synthesis temperature and the geometric surface structure can be noticed. The values of Ra and RMS increase with linear fashion from 0.29 to 0.70 nm and from 0.35 to 0.87 nm, respectively.
Figure 2. Selected roughness parameters (Ra and RMS) of analysed coatings acquired from AFM images. Sparse stipes bars refer to thicker coatings.

For the coatings grown in the presence of TiCl\textsubscript{4}/DMH precursors a sharp increase in roughness parameters after reaching the temperature of 500°C is observed (Ra and RMS higher than 1.0 nm and 1.4 nm, respectively). Large values of standard deviation of roughness parameters for the coating grown at 500°C is directly linked to the presence of conglomerates of considerable size on the surface, what can be seen on Fig. 1. For the same precursor combination the coatings grown at temperatures below 500°C show roughness parameters within the range 0.35 – 0.58 nm (Ra) and 0.43 – 0.71 nm (RMS). The roughness of magnetron sputtered TiN coating is similar to that of ALD-derived TiN using TiCl\textsubscript{4}/MMH precursors at temperature 500°C, namely 0.68 nm (Ra) and 0.84 nm (RMS).

3.2. Mechanical properties
The samples of the first group of coatings (with thickness in the range 10 – 30 nm) are too thin to have directly reliable results by nanoindentation, thus the further analysis of those samples mainly focused on LFM investigation (Section 3.3). From the nanoindentation theory, which says that the depth of penetration should not exceed 10% of the coating thickness, it appears that in the case of indenters whose radius of rounding is less than 20 nm, the coating should have a thickness of approx. 200 nm.

Figure 3. Hardness and elastic modulus values of 80 nm thick TiN coatings with reference to the substrate.
The fulfilment of this condition is necessary and allows to receive real values of mechanical properties with minimized substrate effect on the result [6,7]. In practice, the mechanical properties of coatings of much smaller thickness are successfully determined and the generally accepted limit is approx. 50 nm [8]. The thinner the coating, the smaller the convergence of the obtained result with the actual value. It depends on many factors, including one of the most important relationships between the mechanical properties of the substrate-coating and the superposition of these properties. Due to the imperfect geometry of the used indenters it is recommended to perform measurements on coatings with a thickness of approx. 100 nm [7]. Even after adopting the smallest limiting thickness found in the majority of publications referring to the measurement of ultra-thin coatings, the provided coatings are too thin to be able to determine even comparably changes in their properties. Nevertheless a careful work was done on both, TiCl₄/MMH@420°C and reference magnetron sputtered TiN samples, in order to extrapolate hardness (H) and elastic modulus (E) values. Obtained values (Fig. 3) were supplemented with the results calculated for bare substrate. The ALD-derived TiN exhibited H and E values of 15.5±0.8 GPa and 216±11 GPa, respectively. In case of magnetron sputtered TiN mechanical properties were higher than those of ALD-synthesized TiN and not too different to those found in literature, for TiN produced by other techniques (H=18.7±1.1 GPa, E=242±13 GPa). The smallest values of H and E were achieved for the bare substrate (13.2±0.1 GPa and 184±1 GPa, respectively).

3.3. Tribological properties

In Fig. 4 average values of friction coefficient for all investigated coatings are presented.

![Figure 4. Mean values of friction coefficient for all investigated coatings obtained during LFM experiment. Sparse stipes bars refer to thicker coatings.](image)

From the graph it can be noticed that for ALD-derived samples the values of friction coefficient maintain at similar level (ranging from 0.3 to 0.4) up to annealing temperature of 500°C, independently on precursors used. Increase of the annealing temperature above 500°C results in friction coefficient increase above 0.5. However when compared to the results of reference TiN sample it is clearly seen that magnetron sputtered TiN film is characterized by the highest friction coefficient value (>0.6) amongst all investigated samples. Moreover, taking into account that roughness of the MS-derived TiN is similar to majority of ALD-synthesized TiN coatings, no general correlation of this parameter with the friction coefficient could be found. Thus, it can be suggested that besides topography other factors were present and governed the frictional characteristics of these coatings.
Measurement of H and E (Section 3.2) allowed determination of elastic strain to failure (which is related to H/E) and resistance to the plastic deformation (often associated with $H^3/E^2$) translating directly into the behaviour of coating during wear and scratch tests (assuming uniformity of the coating) [9–13]. Wear behaviour and scratch adhesion of the studied coatings is presented in Table 2, supplemented with results of H/E and $H^3/E^2$ ratios.

Table 2. Wear coefficient and scratch critical load of the studied coatings (80 nm thick) supplemented with corresponding results of H/E and $H^3/E^2$.

| Coating       | Wear coefficient K (mm$^3$/Nm) | Critical load Lc (mN) | H/E  | $H^3/E^2$ (GPa) |
|---------------|--------------------------------|----------------------|------|-----------------|
| TiCl$_4$/MMH@420°C | (1.2±0.9)·10$^{-4}$         | 10.5±0.3            | 0.072| 0.080           |
| MS            | (9.2±1.3)·10$^{-7}$         | 14.6±0.2            | 0.077| 0.111           |

Wear behaviour analysis showed that in case of ALD-derived TiN film the wear coefficient K is more than 2 orders of magnitude higher than for magnetron sputtering sample. A measure of adhesion strength of the coating to the substrate is the load at which total peeling-off of the coating from the substrate surface occurs, denoted here as Lc parameter. The critical loads obtained in nanoscratch tests, for ALD and MS-derived TiN films were 10.5 mN and 14.6 mN, respectively. Comparing the results of wear and scratch resistance with calculated values of H/E and $H^3/E^2$ it can be noticed that presented correlations are consistent with literature. Most of the failure mechanisms begins with the plastic deformation thus the coating should be more resistant to wear when it has a high resistance to plastic deformation and, therefore, it reaches a high value of $H^3/E^2$ (H/E).

4. Conclusions
This paper describes few experimental results of frictional properties of the TiN coatings deposited by atomic layer deposition technology using lateral force microscopy. LFM results revealed that for ALD-derived samples grown at temperature below 500°C the values of friction coefficient maintain at similar and relatively low level (ranging from 0.3 to 0.4) independently on precursors used. Wear and scratch resistance tests results showed correlation with H/E and $H^3/E^2$ ratios to be consistent with literature. Obtained results will constitute basis for the study of tribological properties of MAX phases and MXenes based on nitrides (i.e. TiN) and carbides – novel materials synthesized by the tailored bottom-up growth by means of atomic layer deposition on substrates with different nature with a fine control of the chemical composition and microstructure.

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