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THE INFLUENCE OF NITROGEN CONTENT ON THE MECHANICAL PROPERTIES OF TiN_x THIN FILMS PREPARED BY REACTIVE MAGNETRON SPUTTERING

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Abstract: *The main purpose of this work is to present and to explain the changes of structure and mechanical properties of TiN_x thin films, produced by DC reactive magnetron sputtering, by varying the nitrogen flow rate between 4.5 and 10.5 sccm. The structural characterization results reveal a typical fcc TiN structure with (111) and (222) diffraction peaks. The strongest intensity in the (111) orientation was obtained for samples prepared with low nitrogen flows. For this kind of samples was obtained high values of hardness. The gradual increasing of nitrogen flow brings a decrease in intensity of TiN (111) peaks due to the significant loss of crystallinity. This loss of crystallinity has influenced negatively mechanical properties of films.*

Key words: *titanium nitride, sputtering, structure, hardness*.

1. Introduction

Transition metal nitrides are attractive materials for industrial applications due to their remarkable mechanical and tribological properties including high hardness, high wear resistance and low friction coefficient. For example, most machining tools such as drills, hobs, mills, and cutting inserts are nowadays coated with titanium nitride (TiN_x) to improve the wear resistance and durability of machining tools [9].

Moreover, in order to improve the performance and extend the life of a cutting tool, a among them, the sputtering deposition process has been used in the present work, in order to produce TiN_x thin films due to the higher deposition rate and lower cost. At the same time, this technique is capable of reducing the arcing event which results from charge accumulation on film surfaces. It consequently prevents properties deterioration of films and maintains the deposition process stable. The technique reveals three advantages: higher homologous temperatures, higher ratios of the fluxes of bombarding ions and depositing atoms, and higher energies of bombarding ions [9].

TiN_x thin film is usually used as a protective coating for oxidation resistance [1]. For applications as cutting tools and diffusion barriers, a preferential orientation of a TiN thin film - (111) - can have a significant effect on its performance [4].

A large number of processing techniques such as pulsed laser deposition [4],

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magnetron sputtering [7], cathodic arc evaporation [3], ion beam assisted deposition [8] and chemical vapour deposition [6] have been used to deposit TiN_x thin films.

Different studies in the literature are referring to the deposition of titanium nitride films by sputtering [9], [5].

These studies reported different mechanical and tribological behaviour of titanium nitride films, depending upon the deposition conditions: the substrate bias voltage, the substrate temperature and the nitrogen flow rate. In general, a negative bias voltage and different nitrogen flow is applied to the substrate during deposition to enhance the hardness, adhesion and friction coefficient of the titanium nitride films, attributable to the ion bombardment energy [2].

Taking into account these aspects, the goal of this study was to finding related to the structural evolution as a function of the reactive DC sputtering deposition parameters and the influence of such parameters on the mechanical behaviour of TiN_x thin solid films.

2. Experimental Details

For the present work, TiN_x thin films were deposited onto silicon (100), high speed steel (AISI M2) and stainless steel (AISI 316) substrates, by DC reactive magnetron sputtering, using a laboratory sized deposition chamber which can be found in the Minho University, Department of Physics from Guimaraes Portugal.

Prior to all depositions, the substrates were ultrasonically cleaned and sputter etched for 15 minutes in an argon flow, which was fixed and kept constant at 6 sccm. Depositions were carried out under an Ar/N_2 atmosphere. The working pressure was kept approximately constant at $5x10^{-3}$ mbar during the entire coating deposition process. The nitrogen (reactive) gas flow varied from 4.5 to 10.5 sccm (4.5, 6, 7.5, 9, 10.5 sccm). Samples were placed in a substrate holder, which was set in a simple rotation mode (7 rpm) during the films deposition. The substrate holder was maintained at a temperature of 100 °C for all depositions. The substrates were biased (−50 V) and the deposition time for each sample was 1 h.

Thickness measurements were obtained from Ball-Cratering technique using the Calotest method, while residual stress values were calculated with Stoney's equation using the curvature radii of the stainless steel samples before and after the film depositions.

X-ray diffraction investigations were performed on silicon substrates samples using a Philips PW diffractometer (CuK_α radiation) in a Bragg-Brentano geometry configuration. The resulting patterns were processed with a Pearson VII function in order to obtain the peak characteristics: position, intensity and full width at half maximum (FWHM).

The mechanical characterization (hardness and Young's modulus) were determined from the loading and unloading curves, carried out with an ultra low load-depth sensing nanoindenter - CSM Instruments type, equipped with a Berkovich diamond indenter, operating at a constant approach load rate of 2000 nm/min. up to a maximum indentation depth of 150 nm. The maximum load value was 30 mN, the holding time at maximum depth 5 s and, the unloading rate was 2000 nm/min. For each sample, an average number of 8 indentations were performed.

3. Results and Discussions

3.1. Thickness, deposition rate and target potential

For clear evidence of deposition parameters, thickness and residual stress of the titanium nitride films, in Table 1 are registered a series of experimental results obtained.

Table 1
Reactive gas flows, thickness and residual stress of the produced TiN_x film

Samples	Nitrogen flow [sccm]	Thickness [µm]	Residual stress [GPa]
Ti (1)	4.5	1.5	–1.68
TiN_x (2)	6	1.29	–2.90
TiN_x (3)	7.5	1	–3.56
TiN_x (4)	9	0.98	–0.60
TiN_x (5)	10.5	0.68	–1.87

From this table, it can be seen that the films thickness for the samples decreases continuously (from 1.5 to 0.68 µm) with increasing nitrogen flows. The films revealed low values of residual stress, inferior to 2 GPa and compressive in nature. Only in the case of the samples TiN_x (2) and TiN_x (3) a superior to 2 GPa compressive stress was detected.

Figure 1 presents the evolution of deposition rate and target potential as a function of the reactive gas flow. As readily seen, an increase of the nitrogen flow to 6 sccm provokes a sudden increase of the target potential value, after that, is remarkable unexpected decrease in the target potential values from an nitrogen flow interval from 6 to 10.5 sccm. This behaviour appears may be due to the increase in the overall reactive gas flow, which potentiates the target poisoning effect.

At the same time, from the same figure, it is observed that the deposition rate of the films decreased continuously from around 0.42 x 10^{-4} to 0.17 x 10^{-4} µm/s with increasing of the nitrogen flow from 4.5 to 10.5 sccm.

The reason for this decrease in the deposition rate is that the reactive gas can react with Ti target to form a nitrides compound layer at its surface, which reduces the metal sputtering yield. This is partly due to the poor sputtering capability of nitrogen upon replacing argon and partly from the target poisoning effects (induced by the increasing amount of nitrogen in the chamber) where the sputtering yield for nitride is much smaller than the metal, and partly that these compounds have higher secondary electron emission yields than metal targets [7].

3.2. Structural properties

The experimental results in terms of structural features of TiN_x (on silicon substrates) thin films are presented in Figure 2. In all samples the deposited

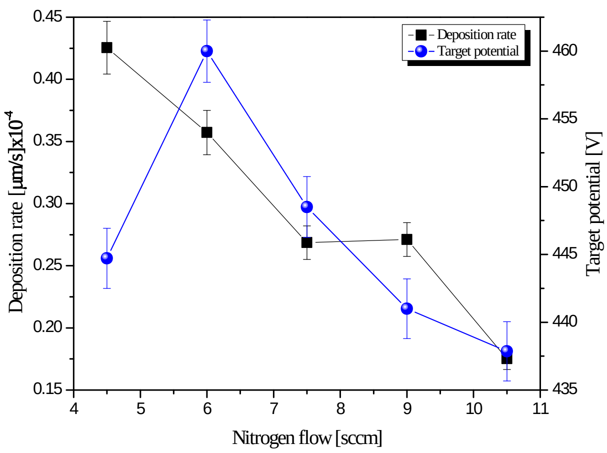

Fig. 1. *Deposition rate and target potential of the produced TiN_x coatings as function of reactive gas flows*

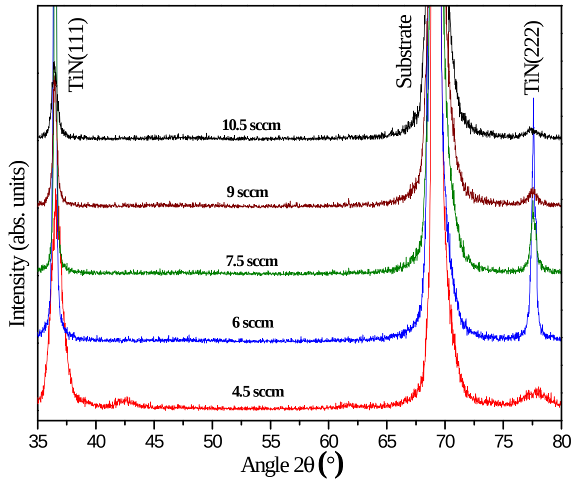

Fig. 2. *X-ray diffraction patterns of the TiN_x films as a function of the reactive gas flows*

coatings showed face-centered cubic (fcc) phase (Fm-3m (225)) of titanium nitride (TiN) (according to the Joint Committee on Powder Diffraction Standards - JPCDS card no. 00-038-1420), oriented with the (111) and (222) directions. Analyzing both peaks of TiN_x with the (111) and (222) orientation, can be observed that with increasing nitrogen flow from 4.5 to 7.5 sccm, the peak-intensity increases, and then decreases with the increasing nitrogen flow up to 10.5 sccm. However, it may be presumed that the intensity of the peak's has small changes, being the most clearly defined in the case of sample produced with a nitrogen flow of 4.5 sccm.

Furthermore, comparing these results with those existing in the literature, it can be concluded that the titanium nitride films retains the same classic orientations the parent compound TiN (111) and TiN (222).

The mean grain size of crystalline fcc phases was calculated by Scherer's equation, in the present work. The increase of the nitrogen flow rate seems to have a big effect on the grain size. Thus, the minimum values of the grain average dimensions were centred around 8-18 nm and corresponding to the samples prepared with nitrogen flows of 4.5, 9 respectively 10.5 sccm. The maximum values of grain dimensions were found to be 44 and 51 nm, belonging to the samples prepared with nitrogen flow in interval 6-7.5 sccm. These major differences of the grain dimensions can be attributed to the increase and decrease in intensity of the peaks which reveals a slowly loss of the films crystalinity with the increasing nitrogen flow.

These changes remarked in the structural behaviours, will have a considerable influence on mechanical properties of the TiN_x thin films.

3.3. Mechanical characterization

Figure 3 presents the evolution of the hardness and elastic modulus as a function of the nitrogen flow. It can be seen that for sample produced with nitrogen flow of 4.5 sccm was obtained the high value of the hardness which corresponds to 18.4 GPa. Obtaining this maximum value of hardness for the TiN_x (1) thin film could be explained in terms of replacement the metallic bond with ion binding during the deposition process. Moreover, small grain sizes (around 8 nm) consisting in the crystallographic lattice of the compound, leading to a

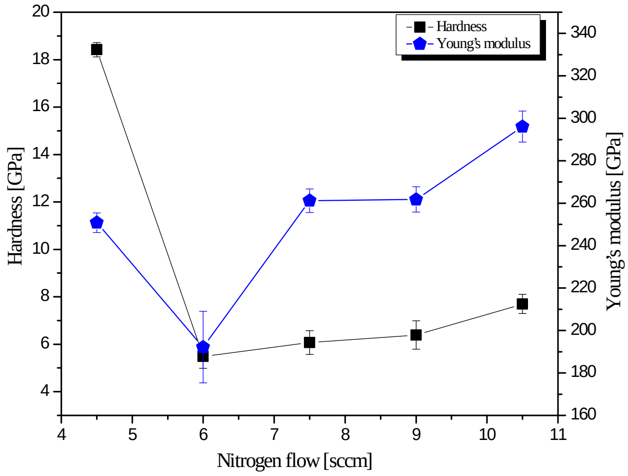

Fig. 3. *Hardness and Young's modulus of sputtered TiN_x films as a function of the nitrogen flow*

densification of the crystallographic arrangement and hence to obtain this high hardness values. In additions, relatively small value of compressive residual stress around - 1.68 GPa was presented in this sample and seems to influence the mechanical properties positively.

The lower value of the hardness - 5.5 GPa - corresponding to the titanium nitride film prepared with the nitrogen flow of 6 sccm. This suddenly decrease in hardness could be explained by looking at the changes of film's thickness (Table 1), target potential and grain size. Actually, the decreasing of film thickness (from 1.5 to 1.29 μm) and poisoned of the Ti target during to the deposition process observed in Figure 1, could contribute to this softening behaviour. In additions, the biggest size of the crystallites (around 51 nm) was found for this kind of film - TiN_x (2).

Moreover, for variation of nitrogen between 7.5 and 10.5 sccm, the coatings present almost the same values of hardness, 6.1 to 7.7 GPa, with a slightly increasing based probably on the decrease of crystallinity, emphasizing the tendency to amortization of the films.

The evolution of the elastic modulus (Young's modulus) of the titanium nitride films present a very similar behaviour as that observed for hardness. Thus, for the nitrogen flow between 4.5-6 sccm, the elastic modulus presents a decreasing; varying from 250 down to 192 GPa and, at higher nitrogen flow, up to 10.5 sccm, there is a significant increase of its value from 261 up to 296 GPa. In the interval of nitrogen 7.5-9 sccm, the values of elastic modulus was kept approximately constant at around 261 GPa. This is characteristic of brittle materials tested by depth sensing indentation. No clear correlation or influence was observed between hardness and films thickness.

4. Conclusions

TiN_x thin films were produced by direct current magnetron sputtering. The thin films were deposited onto high-speed steel, silicon and stainless steel substrates, from a pure Ti target, varying the flow rate of the reactive gas.

In terms of mechanical behaviour, it was found that the most performing TiN_x film was that one with small sized of the grains (around 8 nm), a crystalline structure with fcc phase and strong (111) orientation of the peaks, obtained using the lowest nitrogen gas flow of 4.5 sccm. This sample noted with TiN_x (1) presented a higher value of hardness (18.4 GPa) and a good thickness of 1.5 μm.

With the increase of the nitrogen flow between 4.5 to 10.5 sccm was observed a continuous decrease of the thickness and deposition rate. In additions, the evolution of the target potential reveals for sample prepared with 6 sccm a target poisoning effect during the deposition process. Due to the effect of the poisoning of the target, the deposition rate and mechanical properties was affected, thus obtaining the lowest values of hardness and elastic modulus at around 5.5 and respectively 192 GPa. With increasing nitrogen flows up to 10.5 sccm, the hardness of TiN_x film increased slightly from 6.1 to 7.7 GPa.

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