The influence of the magnetron target state on the mechanical characteristics of hard coatings

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The properties of the hard coatings deposited by PVD methods depend on the processes occurring at the surface of the vapors source (the target), within the plasma generated in the deposition chamber and at the plasma-substrate interface. The most investigated processes were those at the plasma-substrate interface and within the plasma volume. Less attention has been paid in the literature to the processes occurring at the level of the vapors source, although these ones play a decisive role in the reproducibility of thin films characteristics. In this paper the influence of the target condition on the properties of titanium nitride films deposited by using a relatively new method is presented. The deposition technique is a combination between magnetron sputtering and ion implantation (*CMSII*). The target condition during the deposition process is correlated with the evolution of the magnetron discharge impedance. The influence of the reactive gas flow on the impedance of the magnetron discharge was also investigated. As a result, a method for controlling the characteristics of the hard coatings by using the magnetron discharge impedance was established.

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1. Introduction

Transition metal nitrides are very important candidates for industrial applications due to their properties concerning hardness, high temperature resistance and corrosion resistance. Of all nitrides, titanium nitride, produced by PVD or CVD methods, is one of the most investigated coatings. Due to its high deposition rate, magnetron sputtering is a wide used PVD technique, very attractive for scale-up. One of the factors affecting the deposition rate in the reactive sputtering process is the partial pressure of the reactive gas [1]. The deposition rate drops significantly when the partial pressure of the reactive gas exceeds a certain limit. The formation on the target surface of a compound with a lower sputtering yield than of the pure metal is responsible for this phenomenon [1,2].

CMSII technique combines magnetron sputtering deposition and ion implantation. High voltage pulses lead to a densification of the coating with beneficial effects on the properties concerning the microhardness, adhesion and internal stress [3-5]. An increase of the deposition rate up to 4 times in comparison with the conventional magnetron sputtering has been also noticed. [3].

This study is based on the observation that the impedance of the magnetron discharge changes when the reactive gas is introduced into the deposition chamber. Based on the processes occurring at the target surface, a correlation between the discharge impedance and the nitrogen flow rate can be established.

2. Experimental

The typical parameters and the experimental arrangement for *CMSII* technique are given elsewhere [3, 5]. A titanium target with a diameter of 80 mm and a thickness of 8 mm has been used.

The impedance of the magnetron discharge was determined by reading the instantaneous values of the discharge voltage while the discharge current was kept constant. Ten voltage values were periodically read and then an average value was used to calculate the impedance.

The impedance measurements were carried out during the coating process of plain carbon steel samples (C 45) with titanium nitride layers.

The coating was characterized in terms of microhardness using an Epytip microscope with loads of 40 g and 100 g. The sample hardness before coating was 300 HV.

3. Results and discussion

In Fig.1 the configuration of the magnetic induction $B_{\|}$, parallel to the magnetron surface, is shown.

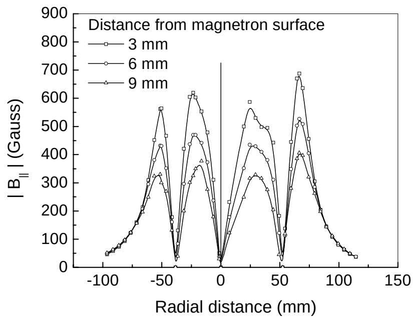

Fig.1. The magnetic field configuration of the magnetron system

Due to this radial magnetic field and axial electric field, the ions will be subjected to a helicoidally movement. Some ions will be trapped in this configuration and they will sputter the target material. In Fig.2 a titanium target after 10 deposition cycles and before deposition is shown.

Fig. 2 The titanium target after and before the deposition process

As it can be seen, the sputtering is not uniform, the maximum sputtering yield corresponding to the maximum value of the magnetic induction.

In Fig. 3 the evolution of the magnetron discharge impedance with the nitrogen flow rate is presented. Initially, this impedance increases with the nitrogen flow rate.

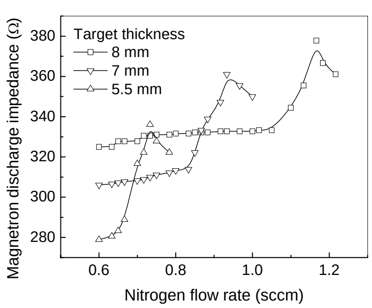

Fig.3 The influence of the nitrogen flow rate on the magnetron discharge impedance

At a certain flow rate the impedance reaches a maximum value and then it drops if the gas flow rate is further increased. This is explained by the increase of the secondary electron yield due to the formation of a compound on the target [6]. The discharge becomes less resistant and the required voltage, necessary to keep a given current, is lower. Another observation is that the maximum value of the impedance shifts to lower values with the decrease of the target thickness.

The maximum value of impedance is related to the transition from metallic to ceramic regime of the magnetron discharge. By using a titanium target, *CMSII* technique usually produces a nanocomposite nc-Ti_2N/nc-TiN coating, with Ti_2N as the dominant phase.

In order to form a stoichiometric structure of the coating, the ratio of the incoming species (titanium and nitrogen) has to be kept constant. Due to the target consumption, the magnetic induction at the target surface increases from a batch to the next one. Consequently, it is expected that the number of charged particles that escape from the magnetic configuration for the same discharge current to be lower. In order to keep an appropriate Ti:N ratio, the nitrogen flow rate should be reduced. If this does not happen, a “poisoning” effect occurs on the target surface and the resulting layers become suprastoichiometric. The coatings obtained at the nitrogen flow rate corresponding to the maximum value of the impedance shows a high hardness, in the range of 4000-5000 HV0.04. A scanning electron microscopy (SEM) image of the coating is shown in the Fig. 4.

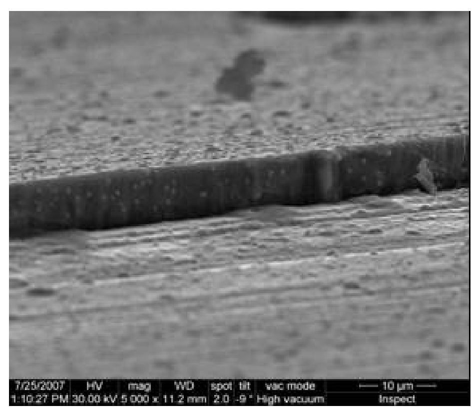

Fig. 4. SEM image of a nc-Ti_2N/nc-TiN coating deposited by CMSII method.

If the nitrogen flow rate is high, the layer became suprastoichiometric, its color is yellow-reddish and the microhardness drops to a value around 1000 HV 0.04. If the nitrogen flow rate is low, the coatings show a dual phase structure consisting in Ti and Ti_2N phases with unsatisfactory mechanical properties.

In Fig. 5a the evolution of the impedance during the deposition process, for a coating produced at a reactive gas flow rate corresponding to a maximum value of impedance, is shown.

A decrease of the impedance during the deposition process occurs. This decrease might be explained by the dimensional modification of the target during the deposition or by the processes occurring on the target surface. In order to clarify this phenomenon, the evolution of the impedance for a coating produced at nitrogen flow rate lower than the optimum value was recorded (Fig.5b). As it can be seen, the impedance remains approximately constant for three hours, the entire duration of the process. This result leads to conclusion that the decrease of the impedance for the coating deposited at the maximum value of the impedance is due to the processes occurred on the surface of the target and not to its dimensional change. If the nitrogen flow rate is higher than the value corresponding to the maximum impedance value, the magnetron discharge impedance remains also relatively constant during the deposition process. One of the most important processes occurring at the target surface seems to be the formation of a compound similar to that deposited on the substrate (titanium nitride). By sputtering, this compound is transferred from the target to the substrate without changing its composition.

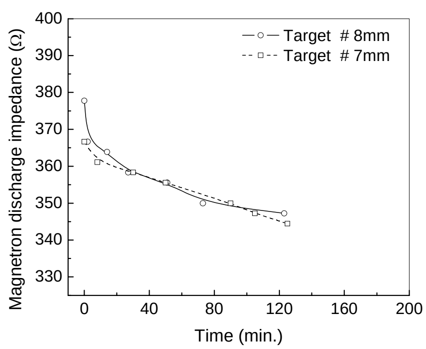

Fig. 5a The evolution of the magnetron discharge impedance at a reactive gas flow rate corresponding to the maximum value of impedance.

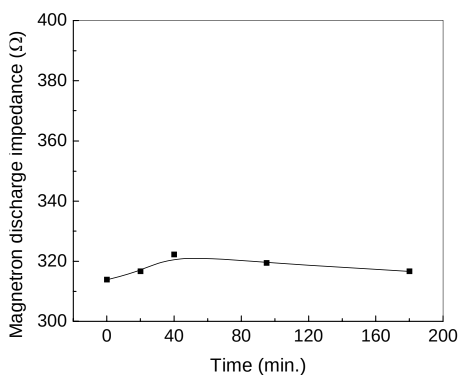

Fig. 5b The evolution of the magnetron discharge impedance at a reactive gas flow rate lower than the maximum value of impedance.

On the other hand, the time-decrease of the discharge impedance seems to indicate an increase of the electron secondary emission coefficient, which might be related with a structure change of the compound formed on the target surface during the deposition process. This change could affect the sputtering coefficient as well and consequently the deposition rate. A decrease of the sputtering rate with increasing nitrogen flow rate over a certain value was already reported in the literature [3].

The phenomenon concerning the formation of a very thin coating on the magnetron target, followed by the transfer of the material from this coating to the substrate was discussed by other authors as well [7], but more investigations are necessary in order to prove that this is the dominant mechanism of coating formation on the substrate.

This mechanism was already demonstrated for plasma nitriding at a current density of more than one order of magnitude lower than the current densities usually used in magnetron sputtering [8].

Formation on the target surface of a thin layer with special characteristics appears to be essential for producing at the substrate level of high quality coatings in terms of structure and hardness.

This condition is rather difficult to be achieved because the target, in the absence of a balance between formation and sputtering of this thin compound, can shift easily from metallic to ceramic regime (or poisoning if the nitrogen flow rate is too high).

4. Conclusions

The investigations carried out so far demonstrated that the magnetron discharge impedance can be an effective instrument in controlling the deposition process for hard titanium nitride coatings.

The formation on the surface of the magnetron target of a very thin coating with special characteristics

seems to play an essential role in producing of hard high quality titanium nitride coatings.

Acknowledgments

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