Nanocharacterization of titanium nitride thin films obtained by reactive magnetron sputtering

V V MERIE¹, M S PUSTAN¹, C BÎRLEANU¹ and G NEGREA²
¹ Technical University of Cluj-Napoca, Faculty of Machines Building, Department of Mechanical Systems Engineering, 103-105 Muncii Avenue, Cluj-Napoca, Romania
² Technical University of Cluj-Napoca, Faculty of Materials and Environmental Engineering, Department of Materials Science and Engineering, 103-105 Muncii Avenue, Cluj-Napoca, Romania

E-mail: Violeta.Merie@stm.utcluj.ro; vio1919@yahoo.com

Abstract. Titanium nitride thin films are used in applications such as tribological layers for cutting tools, coating of some medical devices (scalpel blades, prosthesis, implants etc.), sensors, electrodes for bioelectronics, microelectronics, diffusion barrier, bio-microelectromechanical systems (Bio-MEMS) and so on. This work is a comparative study concerning the influence of substrate temperature on some mechanical and tribological characteristics of titanium nitride thin films. The researched thin films were obtained by reactive magnetron sputtering method. The experiments employed two kinds of substrates: a steel substrate and a silicon one. The elaboration of titanium nitride thin films was done at two temperatures. First, the obtaining was realized when the substrates were at room temperature, and second, the obtaining was realized when the substrates were previously heated at 250 °C. The elaborated samples were then investigated by atomic force microscopy in order to establish their mechanical and tribological properties. The nanohardness, roughness, friction force are some of the determined characteristics. The results marked out that the substrate which was previously heated at 250 °C led to the obtaining of more adherent titanium nitride thin films than the substrate used at room temperature.

1. Introduction
The development of new materials and new technologies is needful in order to meet the growing necessities of the customers. A special attention must be paid to the link between the structure, the processing and the properties of the materials studied for a specific application. Some researchers aimed at studying the titanium nitride due to its wide range of properties. A low friction coefficient, good resistance to corrosion, high hardness, good adhesive wear, high electrical conductivity, high evaporation temperature, biocompatibility and chemical and metallurgical stability are some of the most important characteristics of titanium nitride [1-9].

The properties mentioned above make titanium nitride suitable for applications within the biomedical, space, microelectronics, cosmetics industries and so on [10-16]. One of the applications is the fabrication of miniaturised devices such as microelectromechanical systems (MEMS). The high melting point and the covalent bonding represent two difficulties that hinder the elaboration of such materials by forming and sintering [11]. Chung-Fon Hsieh and his co-workers reported the use of...
titanium nitride for manufacturing a micro-gap discharge device. In this case, titanium nitride acts as a robust electrode in the device previously mentioned [12].

A widely used application of titanium nitride is that of coating material such as diffusion barrier in the microelectronics industry, hard and protective coatings for the mechanical tools or decorative coatings [13]. Machunze and Janssen studied the use of titanium nitride as diffusion barrier layers in integrated circuit (IC) technology or as wear protective coatings [14]. A cosmetic gold-coloured purposes and wave length selective transparent optical films are other applications of titanium nitride coatings [15]. According to Lawand and his co-workers, titanium nitride is also used in the biomedical industry as coatings of some medical devices such as scalpels [16].

The researchers tried to elaborate titanium nitride thin films through different methods. Plasma-assisted CVD (Chemical Vapour Deposition), magnetron sputtering, RF reactive sputtering, reactive evaporation, laser ablation, electron cyclotron resonance (ECR), PVD (Physical Vapour Deposition), ion-beam deposition, arc deposition are some techniques that were employed for the deposition of titanium nitride thin films on different substrates [10, 15].

The present research is a study concerning the influence of two different parameters on the tribological and mechanical properties of some titanium nitride thin films obtained by reactive magnetron sputtering. The two parameters whose influence was attended are: the material of the substrate and the temperature of the substrate (the temperature at which the deposition of the thin films was done).

2. Materials and experimental procedure

2.1. Materials

Two different materials were employed for the substrates on which the deposition of titanium nitride thin films was realized. First, titanium nitride coatings were deposited on silicon Si (100) substrate. After that a X30WCrV9-3 tool steel was used as material for the substrate. The chemical composition of the tool steel used is given in table 1.

| Steel          | Chemical composition (%) |
|---------------|---------------------------|
|               | Carbon | Silicon | Manganese | Chromium | Vanadium | Tungsten |
| X30WCrV9-3    | 0.25±0.35 | 0.10±0.40 | 0.15±0.45 | 2.50±3.50 | 0.30±0.50 | 8.50±9.50 |

The obtaining of titanium nitride thin films was done using a titanium target with purity of 99.95 %. The process took place in an atmosphere formed by a mixture of argon and nitrogen.

2.2. Experimental procedure

The deposition of titanium nitride thin films was obtained by reactive magnetron sputtering method. The experiments started with the preparation of the substrates. For that purpose, the tool steel substrates were first heat treated (hardened) at 1150 °C in oil and then they were annealed at 600 °C for an hour.

After that the substrates (both the silicon and the tool steel surfaces) were cleaned and washed with acetone and isopropyl alcohol. Then they were introduced in an ultrasonic bath for removing any possible remaining impurities.

The reactive magnetron sputtering process of titanium nitride coatings was realized providing the following conditions and parameters:

- target material: titanium with a purity of 99.95 %;
- atmosphere: mixture of argon and nitrogen;
- atmosphere pressure: 1 mtorr;
- discharge current: 350 mA;
substrate bias: - 40 V;
nitrogen flow rate: 1.2 cm$^3$/min;
deposition time: 17 minutes.

The deposition of titanium nitride thin films was carried out at two different temperatures in order to study the influence of deposition temperature on the obtained layers. For that purpose, some layers were deposited on substrate at room temperature, while the rest were obtained on substrates that were previously heated at 250 °C.

The following notation was established for the obtained samples in order to facilitate the interpretation of the results: “Substrate material _ Deposition temperature” (table 2). “RT” stands for room temperature.

### Table 2. The notation of the investigated samples.

| Sample   | Substrate material | Deposition temperature (°C) |
|----------|--------------------|-----------------------------|
| Steel_RT | X30WCrV9-3         | Room temperature            |
| Steel_250| X30WCrV9-3         | 250                         |
| Silicon_RT| Silicon (100)     | Room temperature            |
| Silicon_250| Silicon (100)     | 250                         |

The as-obtained samples were characterized from the mechanical and tribological point of view at nanoscale. The nanocharacterization of the researched materials was realized using two kinds of microscopes: a NT 206 and a XE 70 atomic force microscope respectively. The tests carried out on the NT 206 atomic force microscope with a n-silicon CSC38 cantilever were done when relative humidity was 19 %, temperature was 25 °C and scanning frequency was 0.7 Hz. The tribological characteristics of studied samples were determined with this kind of microscope. The tests performed with the XE 70 atomic force microscope for determining the mechanical properties employed a silicon nitride cantilever. Its characteristics are: cantilever stiffness of 144 N/m, tip radius of 25 nm, tip height of 109 μm, tip thickness of 24 μm and cantilever length of 782 μm respectively. The XEI Image Processing Tool for SPM data used the Oliver and Pharr method for the interpretation of the obtained data.

### 3. Theoretical formula

The determination of tribological properties implied among other things the determination of friction force. This parameter can be calculated based on the data provided by the atomic force microscope as follows [17, 18]:

$$F_f = \frac{d_z \cdot r \cdot G \cdot h^3 \cdot b}{l^2 \cdot s}$$

where $d_z$ represents the tips deflection, $r$ is a constant ($r = 0.33$), $G$ is shear modulus (for silicon: $G = 53.9 \cdot 10^{-3}$ N/μm$^2$), $h$, $b$ and $l$ are the dimensions of the cantilever, while $s$ is tips height ($s = 18$ μm). The values of tips deflection are taken from the data offered by the program used for interpreting the images taken by the Surface Scan program. Data processing was performed using the Surface Explorer program.

According to the data given by the producer, the dimensions of the cantilever used for investigations are:

- thickness: $h = 1$ μm;
- width: $b = 32.5$ μm;
- length: $l = 350$ μm.

### 4. Results and discussions

The topography of the obtained titanium nitride thin films on both steel and silicon substrates was studied by atomic force microscopy. The 3D images obtained for the samples deposited on steel and silicon surfaces at 250 °C are presented in figure 1. The samples obtained on silicon substrates shows much smoother surfaces as the samples obtained on steel substrates.
The roughness of the studied samples was determined based on the data given by the NT 206 atomic force microscope in order to characterize the surfaces of the elaborated thin films. Its fluctuation for all four kinds of samples is graphically given in figure 2. When the samples were elaborated on the same substrate (either steel or silicon), the preheating the substrate led to the decrease of thin films roughness. Taking into account the average value determined for this parameter, the decrease of this parameter was about 18 % for the samples deposited on steel substrates and 22 % for the samples deposited on silicon substrates respectively. Regarding the influence of deposition temperature, the average values of roughness for the samples elaborated at room temperature were relatively equal, while the average values of roughness for the samples elaborated at 250 °C varied in the sense that the samples deposited on steel surfaces were characterized by a roughness higher with almost 6 % than the samples elaborated on silicon surfaces. The higher values for surface parameter were marked out for the samples deposited on steel substrate at room temperature, while the smallest values were determined for the samples deposited on silicon substrate at 250 °C.

Concerning the friction force, the fluctuation of this parameter for the researched samples is presented in figure 3. When the samples were deposited on the same surface, the use of substrate preheating determined a significant increase of friction force for both steel and silicon substrates. Thus this increase for the samples elaborated on steel substrate was about 30 % while the increase for the samples elaborated on silicon substrate was about 24 %. As regards substrate influence on the friction parameter of studied titanium nitride thin films, the samples elaborated on silicon surface were
determined to be characterized by a higher value of friction force both for the samples deposited at room temperature and 250 °C respectively. When the deposition was realized at room temperature, the friction force was about 15 % higher for the samples elaborated on silicon surfaces. The same effect was highlighted when deposition temperature was 250 °C, the increase of friction force being about 10 %. The higher values for the friction parameter were determined for the samples deposited on silicon substrates at 250 °C while the smallest values were marked out for the samples deposited on steel substrates at room temperature.

The determination of the nanohardness for the studied titanium nitride thin films was another aim of the present research. The tests carried out for that purpose highlighted a significant influence of substrate and its deposition temperature on the nanohardness of researched coatings. Figure 4 presents the fluctuation of nanohardness for all kinds of researched samples. The preheating of the substrate at 250 °C led to the increase of this parameter for the samples deposited on steel and silicon surfaces with 41 % and 19 % respectively. The values of nanohardness for the samples deposited on silicon substrate were determined to be higher with 62 and 37 % respectively when the deposition was realized at room temperature and 250 °C respectively. The smallest and the biggest values of this parameter were established for the samples elaborated on steel substrate at room temperature and the samples elaborated on silicon substrate at 250 °C respectively.

Figure 3. Friction force of titanium nitride thin films obtained by reactive magnetron sputtering.

Figure 4. Nanohardness of titanium nitride thin films obtained by reactive magnetron sputtering.
5. Conclusions
Concerning the nanocharacterization of titanium nitride thin films obtained by reactive magnetron sputtering on silicon and steel substrates at two different temperatures, we can conclude that:

- the substrate and the its deposition temperature have an important effect on the properties of the elaborated thin films;
- the preheating of substrate at 250 °C leads to the decrease of thin films roughness both for steel and silicon substrate; the smallest and the biggest values of roughness were marked out for the titanium nitride thin films deposited on silicon surfaces at 250 °C and the thin films deposited on steel surfaces at room temperature respectively;
- the titanium nitride coatings obtained on the substrates previously heated at 250 °C are characterized by a better adherence in regard to the thin films obtained at room temperature;
- the preheating of the substrates at 250 °C leads to the increase of friction force for the samples obtained on both steel and silicon surfaces; the biggest values of friction parameter were determined for the thin films deposited on silicon surfaces at 250 °C;
- the nanohardness of samples obtained either on steel or silicon surfaces increases when the substrate is preheated at 250 °C; when the deposition temperature is kept constant, the samples deposited on silicon surfaces are characterized by higher values of the nanohardness than the samples deposited on steel surfaces;
- the temperature of 250 °C was established to be the optimal temperature for obtaining titanium nitride thin films by reactive magnetron sputtering.

6. References
[1] Yazdani A, Soltanieh M, Aghajani H and Rastegari S 2011 Vacuum 86 131
[2] Karagkiozaki V, Logothetidis S, Kalfagiannis N, Lousinian S and Giannoglou G 2009 Nanomed. Nanotechnol. Biol. Med. 5 64
[3] Vasu K, Ghanashyam Krishna M and Padmanabhan K A 2011 Thin Solid Films 519 7702
[4] Serban V A, Rosu R A, Bucur A I and Pascu D R 2013 Appl. Surf. Sci. 265 245
[5] Subramanian B, Ashok and Jayachandran M 2008 Appl. Surf. Sci. 255 2133
[6] Po-Jui Su and Haochih Liu B 2013 Thin Solid Films 529 317
[7] Cui X, Yu Z, Ma M and Chu P K 2009 Surface & Coatings Technology 204 418
[8] Borah S M, Pal A R, Bailung H and Chutia J 2008 Appl. Surf. Sci. 254 5760
[9] Jeyachandran Y L, Narayandass Sa K, Mangalaraj D, Areva S and Mielczarski J A 2007 Mat. Sci. Eng., A 445–446 223
[10] Hussain T, Ahmad R, Khan I A, Siddiqui J, Khalid N, Bhatti A S and Naseem S 2009 Nucl. Instrum. Methods Phys. Res., Sect. B 267 768
[11] Sanchez O, Hernandez-Velez M, Navas D, Auger M A, Baldonedo J L, Sanz R, Pirotta K R and Vazquez M 2006 Thin Solid Films 495 149
[12] Hsieh C F and Jou S 2006 Microelectron. J. 37 867
[13] Bavadi R and Valedbagi S 2012 Materials Physics and Mechanics 15 167
[14] Machunze R and Janssen G C A M 2009 Thin Solid Films 517 5888
[15] Kim S H, Park H, Lee K H, Jee S H, Kim D J, Yoon Y S and Chae H B 2009 Journal of Ceramic Processing Research 10(1) 49
[16] Lawand N S, French P J, Briaire J J and Frijns J. H. M. 2012 Procedia Eng. 47 726
[17] Merie V, Pustan M and Birleanu C 2013 ACTA Technica Napocensis. Series: Applied Mathematics and Mechanics 56(IV) 709
[18] Pustan M, Rochus V, Wu L, Noels L and Golinval J C 2010 ECNF First European Conference on Nanofilm (Lieg, Belgium)

Acknowledgments
This work was supported by the Space Technology and Advanced Research Grant STAR 2012, project number 30036 (REDEMS).