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The influence of substrate temperature on the tribo-mechanical properties of chromium nitride thin films

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Abstract. Different nitrides such as titanium nitride, chromium nitride and so on are used in a widespread range of applications such as cutting tools, medical implants, and microelectromechanical devices and all that due to their mechanical, physical and chemical properties. The aim of this study is to obtain chromium nitride thin films and to characterize them by atomic force microscopy investigations. The chromium nitride thin films were deposited by reactive magnetron sputtering on silicon substrates. During the deposition process, the discharge current, the argon and nitrogen flows, the pressure inside the chamber and the deposition time were kept constant. A chromium target with a purity of 99.95 % was used. Some of the films were deposited after a chromium buffer layer was previously deposited on the silicon substrate. The deposition was carried out when substrate temperature was at room temperature, at 300 and 500 °C respectively. Once the films were deposited, atomic force microscopy investigations were performed in order to emphasize the influence of the substrate temperature on the topographical, mechanical and tribological characteristics. The results pointed out an important influence of the substrate temperature on topographical, mechanical and tribological properties of the investigated chromium nitride thin films.

1. Introduction

Nowadays the interest of researchers in developing new materials and new technologies for obtaining these new materials is growing so that the increasing need of consumers is satisfied. Different types of nitrides such as titanium nitride [1-5], chromium nitride [6-10], and niobium nitride [11-15] and so on are used for applications such as cutting tools, decorative and protective coatings in the automotive industry, microelectronics, biomedical or aeronautical industries, diffusion barrier in microelectronics etc. The use of these kinds of materials is due to their chemical, mechanical, electrical and tribological properties [1, 16]. The characteristics of these ceramics can be obtained by direct current (DC) or radio- frequency (RF) magnetron sputtering [1, 3, 6, 12, 16], laser ablation [4], ion beam assisted deposition [5] and vacuum arc plasma deposition [8] and so on.

Chromium nitride awakes researcher interest for MEMS applications due to its good chemical, wear and corrosion resistance, its good thermal stability, high hardness and so forth [6, 7]. Chromium nitride thin films can be used in corrosive and high temperature environments where titanium nitride thin films cannot be used because of its smaller temperature resistance [8]. One of the most used technologies to elaborate such films is magnetron sputtering [6, 7, 17, 18, 19] due to its high deposition rate, its possibility to control the deposition process and due to the low temperature of the substrate during the deposition. Controlling the substrate temperature, the argon and nitrogen flows, the pressure inside the deposition chamber, the current discharge, the distance between the target and the substrate or the deposition time allows the obtaining of chromium nitride thin films characterized by superior mechanical and tribological properties.

The goal of this research is to elaborate chromium nitride thin films by reactive magnetron sputtering when using different substrate temperatures and to characterize them by atomic force microscopy investigations. The results will allow to determine the influence of substrate temperature on the topographical, mechanical and tribological properties of the deposited chromium nitride thin films.

2. Materials and experimental procedure

2.1. Materials

The chromium nitride thin films were deposited on silicon Si (100) substrates. The deposition process employed a chromium target with a purity of 99.95 %. The atmosphere inside the deposition chamber contained a mixture of argon and nitrogen.

2.2. Experimental procedure

The reactive magnetron sputtering technology was employed in order to deposit the chromium nitride thin films on the silicon substrate. After the substrates were cut in square shape having a surface of 1 cm x 1 cm, they were cleaned in an ultrasonic bath with isopropyl alcohol in order to remove any probable impurities. Then they had been blown with compressed air before introducing them into the deposition chamber.

The deposition process took place in a chamber of the reactive sputtering facility with a Varian TV551 turbo-molecular pump under an atmosphere of high vacuum. The pressure inside the chamber was 1.8 mtorr and the discharge current was 300 mA. The argon and the nitrogen flows were kept constant at 30 cm^3/min and 4.5 cm^3/min, respectively. The distance between the target and the substrates was 60 mm. The films were deposited for 15 minutes. A control specimen was deposited at room temperature directly on the silicon substrates. The rest of the samples were elaborated after a chromium buffer layer had been first deposited on the silicon substrates. The deposition of chromium nitride thin films was realized at three different temperatures in order to study the influence of substrate temperature on the topographical, mechanical and tribological properties of the deposited films. On these lines some films were deposited on substrates with a chromium buffer layer at room temperature, some were deposited on substrates that were preheated at 300 ºC while the rest were obtained on substrates that were previously heated at 500 °C. When the deposition was carried out at 300 ºC and 500 ºC, these temperatures were kept constant during the process. An increase of the temperature up to about 60 ºC was marked out even when the films were deposited at room temperature due to the contact with the plasma. The notation of the deposited films as well as the conditions they were deposited are given in table 1.

Table 1. The notation and the deposition parameters of the elaborated chromium nitride thin films.

Sample notation	Substrate temperature (ºC)	Presence/absence of a chromium buffer layer
CrN-Crbl_rt	20	Without chromium buffer layer
CrN+Crbl_rt	20	With chromium buffer layer
CrN+Crbl_300	300	With chromium buffer layer
CrN+Crbl_500	500	With chromium buffer layer

Then the so-deposited films were characterized from the topographical, mechanical and tribological point of view at nanoscale by atomic force microscopy investigations. A XE 70 atomic force microscope was employed. The tests were performed at a relative humidity of 31 %, while the temperature was of 23 °C. The scanning frequency was 1 Hz and the set point was 5 μN. The indentation tests were carried out using a TD 21562 nanoindenter. As the manufacturer mentioned, the characteristics of this nanoindenter are:

- cantilever stiffness: 144 N/m;
- tip radius: smaller than 25 nm;
- tip height: 109 μm;
- tip thickness: 24 μm ;
- cantilever length: 782 μm.

The interpretation of the obtained data in order to determine the values of the modulus of elasticity and hardness was realized with the XEI Image Processing Tool for SPM (Scanning Probe Microscopy) data using both the Oliver and Pharr and the Hertzian models.

3. Theoretical formula

The friction force was determined in order to characterize the deposited thin films from the tribological point of view. The values of this parameter were calculated using the formula [16]:

$$F_f = \frac{d_z \cdot r \cdot G \cdot h^3 \cdot b}{l^2 \cdot s} \tag{1}$$

where F_f represents the friction force, d_z is the deflection of the tip, r is a constant (r = 0.33), G is the shear modulus of the tip ($G=83\cdot10^{-3}$ N/μm^2), s is tip height and h, b and l are the dimensions of the cantilever. These dimensions, according to the data provided by the manufacturer, are given in the previous section (Materials and experimental procedure)..

4. Results and discussion

Once the films were deposited, the goal of the research was to characterize them in order to determine the topographical, tribological (friction force) and mechanical properties (hardness, modulus of elasticity). The obtained results helped to establish the influence of the substrate temperature on the characteristics mentioned above.

4.1. Topographical characterization

3D images of the four kinds of chromium nitride thin films achieved with the XE 70 atomic force microscope and interpreted with the XEI software are presented in figure 1. The films deposited at room temperature with or without chromium buffer layer and the films deposited when the substrates were preheated at 300 ºC present smoother surfaces than the films deposited on substrates at 500 ºC.

The topographical characterization implied, among other things, the determination of roughness parameters, including the average roughness, R_a. The values of this parameter were determined using the XEI software on the data acquired with the atomic force microscope. Each sample was investigated in five different areas. The fluctuation of the topographical parameter for all types of deposited chromium nitride thin films is graphically given in figure 2. The results pointed out that when depositing the films at room temperature, the addition of a chromium buffer layer on the silicon substrate leads to the increase in the average roughness with about 30 %. When the chromium nitride thin films were elaborated after a chromium buffer layer had been first deposited, the increase of substrate temperature determines an important increase of this topographical parameter. For that purpose, the films deposited at 500 ºC show an average roughness of almost 16 times higher than the films deposited at room temperature. Analyzing the 3D images (figure 1) and the obtained values for the topographical parameter (figure 2), we can affirm that the films elaborated at 500 ºC shows the highest variation of the average roughness. The smallest value of the average roughness was

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determined for the chromium nitride thin films deposited directly on the silicon substrate at room temperature while the highest value is specific to the chromium nitride thin films deposited after a chromium buffer layer was first deposited and the substrate temperature is of 500 ºC.

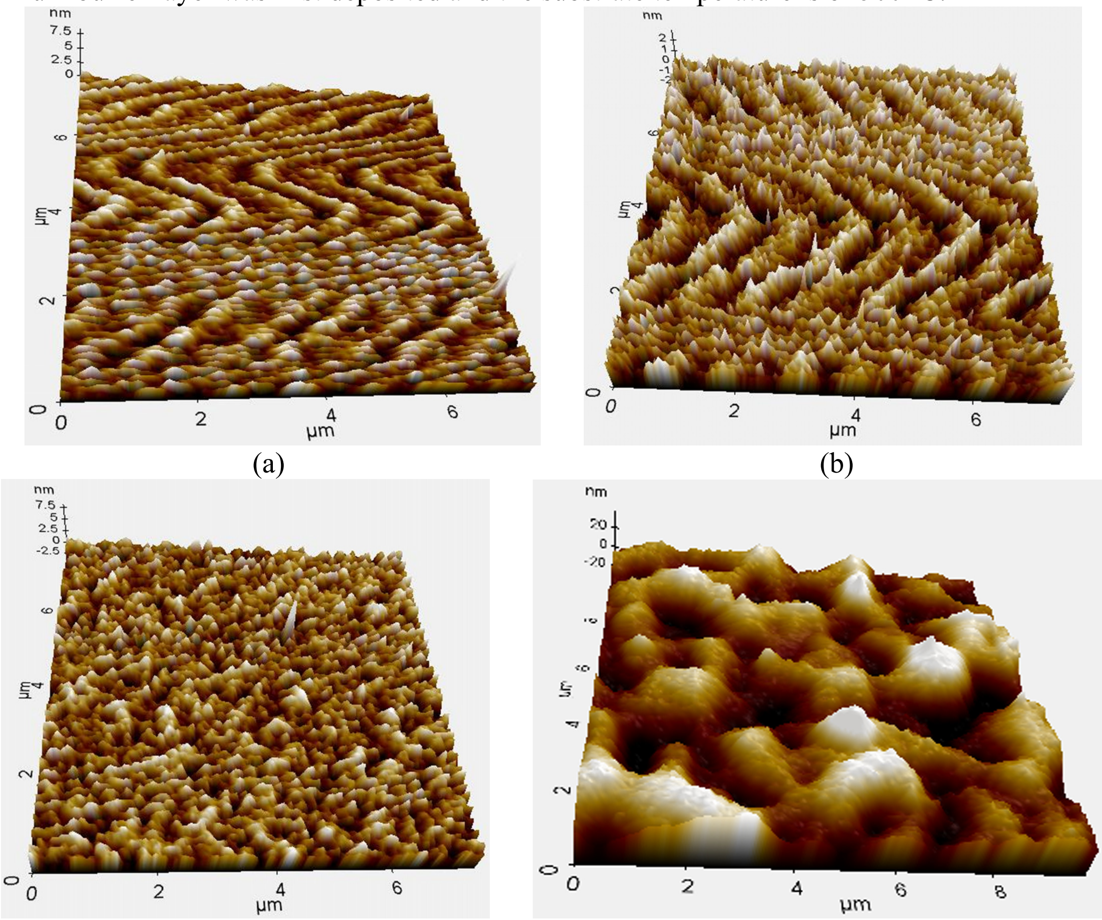

Figure 1. 3D images of deposited chromium nitride thin films: (a) CrN-Crbl_rt, (b) CrN+Crbl_rt, (c) CrN+Crbl_300, (d) CrN+Crbl_500.

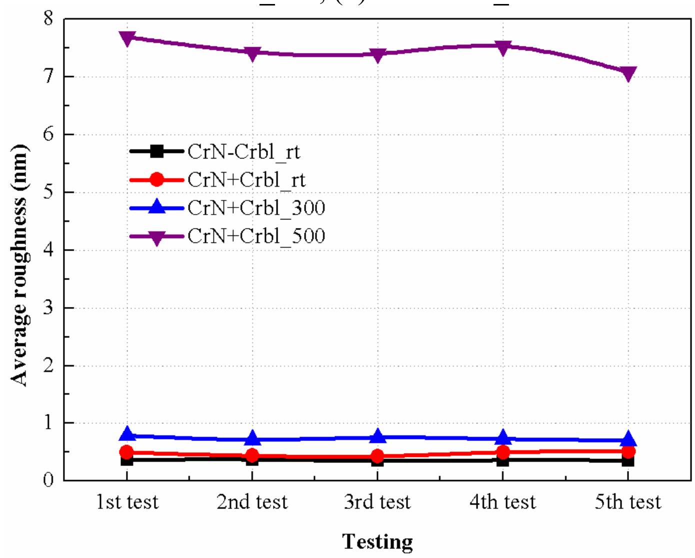

Figure 2. The fluctuation of average roughness for the elaborated chromium nitride thin films.

4.2. Tribological characterization

The tribological characterization of the researched thin films consisted in determining the friction force between the deposited thin films and the tip of the cantilever used when testing the samples. The values of the friction parameter were determined calculating them with the equation (1). The fluctuation of friction force for the four kinds of chromium nitride thin films is presented in figure 3. When the films were obtained at room temperature, the depositing of the chromium buffer layer determined the increase of the friction force by more than 70 % (from 2.6 nN to 4.49 nN). Further the increase of the substrate temperature when the deposition of chromium nitride was done on the chromium buffer layer caused the decrease of the friction parameter of about 2.3 times. Close values of the friction force were determined for the thin films deposited on the silicon substrate at room temperature and those deposited on the chromium buffer layer at 300 ºC. The chromium nitride thin film deposited in the presence of a chromium buffer layer at 500 ºC is characterized by the smallest value of the friction force while the highest value for this parameter was determined on the chromium nitride thin film deposited in the presence of a chromium buffer layer at room temperature.

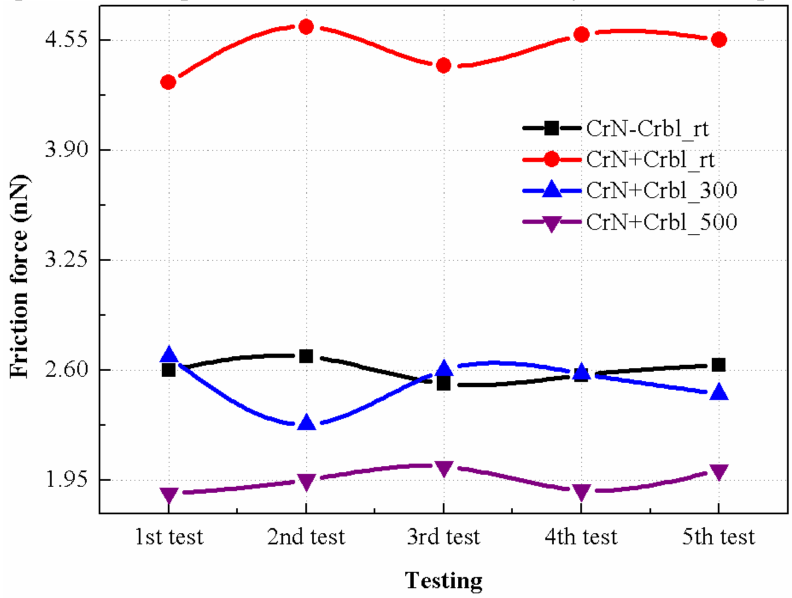

Figure 3. The fluctuation of friction force for the deposited chromium nitride thin films.

4.3. Mechanical characterization

The nanoindentation tests allowed to determine the hardness and the modulus of elasticity of the deposited chromium nitride thin films. The determination of the mechanical characteristics was realized by interpreting the force vs. Z scan curves using the XEI Image Processing Tools for SPM Data (figure 4). The interpretation employed both the Oliver and Pharr model and the Hertzian model. The first model helps us to determine the hardness of the investigated films while the Hertzian model leads to the determination of the modulus of elasticity. The second model is used because it assumes that plastic deformation does not occur between the films and the tip of the cantilever.

Figure 5 graphically presents the average hardness determined for each chromium nitride thin film. First when depositing a chromium buffer layer on the silicon substrate, the value of the hardness increases with about 5 % (from 1.13 GPa to 1.19 GPa). Thereafter the increase of substrate temperature from room temperature up to 500 ºC determines the decrease in hardness with about 37 % (from 1.19 GPa to 0.75 GPa). The chromium nitride thin film deposited on a chromium buffer layer at room temperature is characterized by the highest value of the hardness while the chromium nitride thin film deposited on a chromium buffer layer at 500 ºC presents the smallest value of this mechanical property.

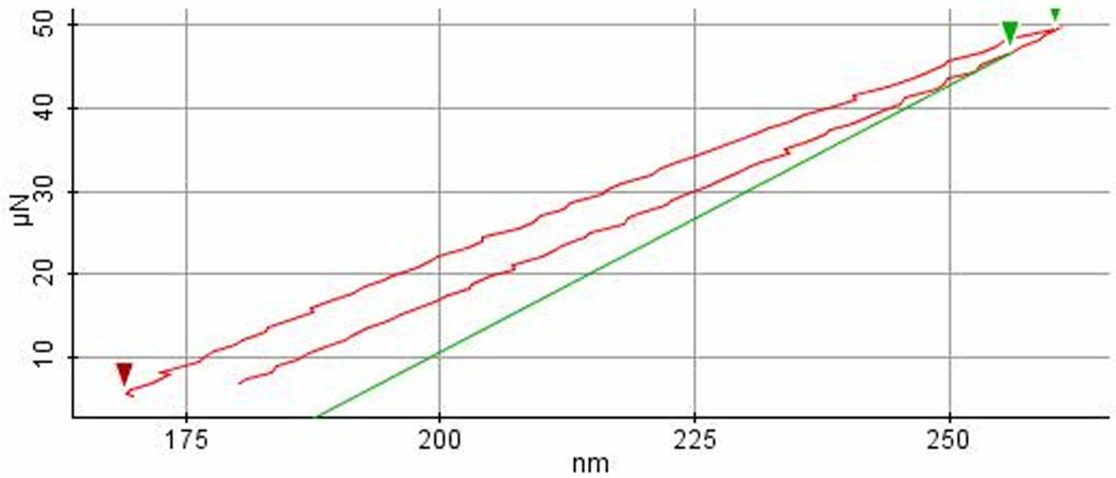

Figure 4. The force vs. Z scan curve for the CrN-Crbl_rt thin film used for determining the hardness and the modulus of elasticity.

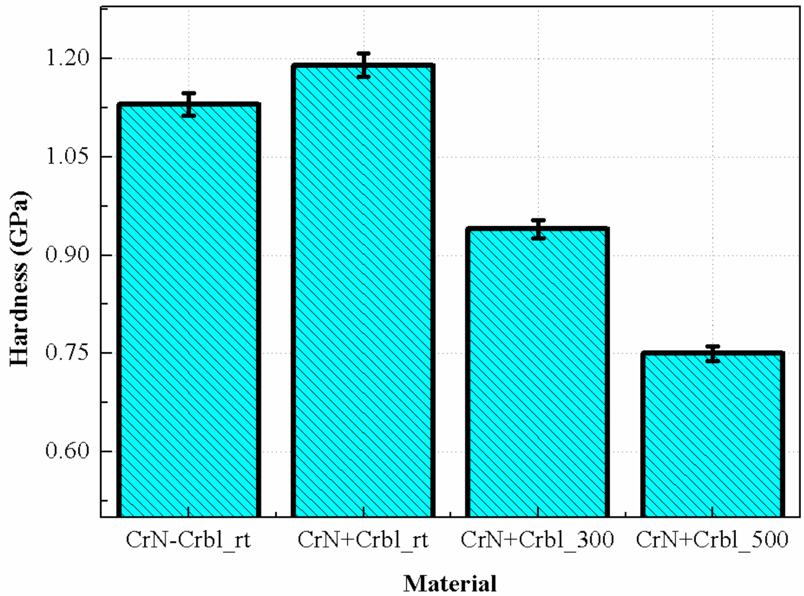

Figure 5. The hardness of the deposited chromium nitride thin films.

The average modulus of elasticity of the investigated chromium nitride thin films is given in figure 6. A similar trend as for the hardness of these samples was noticed. If the increase of the hardness was about 5.3 % (from 1.13 GPa to 1.19 GPa) when depositing a chromium buffer layer at room temperature, the modulus of elasticity in the same conditions increases only with about 3.2 % (from 11.76 GPa to 12.14 GPa). Further as the substrate temperature increases up to 500 ºC, the modulus of elasticity of the deposited films decrease with almost 7 %. This decrease of the modulus of elasticity is not as strong as that of the hardness. The highest value of the modulus of elasticity was determined on the chromium nitride thin films deposited in the presence of a chromium buffer layer at room temperature while the smallest value of this mechanical characteristic was pointed out on the chromium nitride thin films deposited in the presence of a chromium buffer layer at 500 ºC.

We assume that the change in the topographical, mechanical and tribological properties is due to the preferential growing of the films after certain plans. This preferential growing is the result of changing the condition in which the deposition is done: both by depositing the chromium buffer layer on the silicon substrate and increasing the substrate temperature.

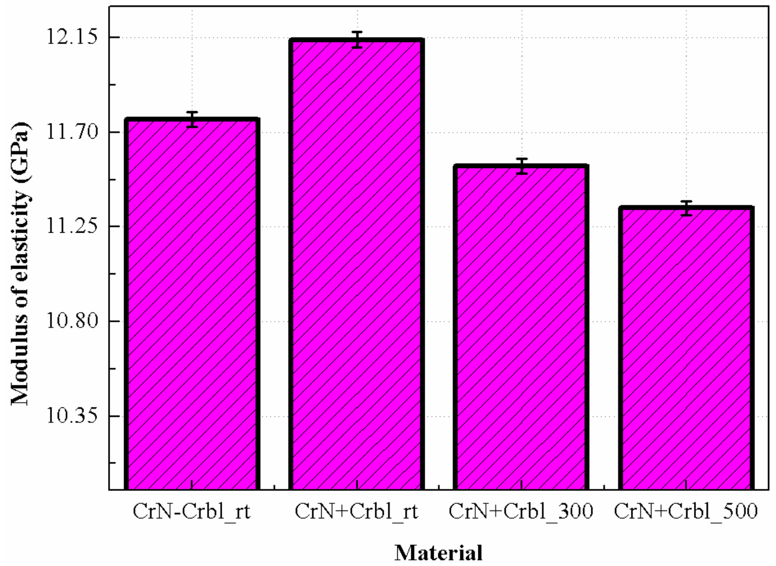

Figure 6. The modulus of elasticity of the elaborated chromium nitride thin films.

5. Conclusions

Chromium nitride thin films were deposited on silicon substrates by reactive magnetron sputtering. Some of the films were deposited after a chromium buffer layer had been first deposited on the silicon substrate. The deposition was realized at three different temperatures namely room temperature, 300 ºC and 500 ºC respectively. The atomic force microscopy investigations were performed on the deposited films. The presence of the chromium buffer layer on the silicon substrate leads to the increase in average roughness. The increase of the substrate temperature up to 500 ºC also determines the increase of the analysed topographical parameter. When elaborating the chromium nitride at room temperature, the deposition of a chromium buffer layer on the silicon causes the increase of the friction force. The friction parameter decreases when increasing the substrate temperature in the case of the films deposited in the presence of the chromium buffer layer. As regards the hardness and the modulus of elasticity of these films, the deposition of the chromium buffer layer on the silicon substrate determines a small increase of both mechanical parameters. A stronger decrease of both the hardness and the modulus of elasticity is perceivable when increasing the substrate temperature up to 500 ºC. The change of the determined topographical, mechanical and tribological properties is due to the preferential growing of the investigated films. Further research will aim at characterizing these chromium nitride thin films from the structural and optical point of view as well as determining the optimal deposition parameters that will lead to a superior mechanical and tribological behaviour.

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