TRIBOMECHANICAL CHARACTERISTICS OF CHROMIUM NITRIDE THIN FILMS DEPOSITED AT DIFFERENT PARAMETERS

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Abstract. Different nitride thin films are widely used in applications for cutting tools, biomedicine, and microelectronics and so on. This study is a research on chromium nitride thin films deposited by direct current magnetron sputtering at different deposition parameters. The coatings were deposited on silicon substrates at different nitrogen flows, pressures and substrate temperatures. Atomic force microscopy investigations were performed to highlight the influence of the previously mentioned parameters on the mechanical and tribological characteristics of the obtained films. The results pointed out a continuous decrease of the modulus of elasticity and a fluctuant variation of the friction force and the nanohardness when increasing the pressure. A fluctuant variation was also marked out regarding the effect of substrate temperature on the mechanical properties. Instead the friction force decreases when the substrate temperature is increased whatever nitrogen flow was employed. The change in mechanical and tribological properties is due to the different preferential orientations after which the films are growing. A nitrogen flow of 2 $cm^3 \cdot min^{-1}$ led to the obtaining of chromium nitride thin films after the (200) orientation. The increase of nitrogen flow and substrate temperature resulted in obtaining chromium nitride films after multiple preferential orientations.

Key words: chromium nitride, DC reactive magnetron sputtering, nitrogen flow, pressure, nanoindentation.

1. INTRODUCTION

Different nitride coatings such as titanium nitride [1,2], niobium nitride [3,4], copper nitride [5,6], titanium-chromium nitride [7,8] and so on are still awaking the interest of the researcher due to their physical, chemical, mechanical, electrical

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Ro. J. Techn. Sci. – Appl. Mechanics, Vol. 64, N° 1, P. 57–72, Bucharest, 2019

and/or optical properties. This interest is furthermore justified by the fact that these properties can satisfy the growing requirements of different categories of consumers. Chromium nitride is one type of nitrides used for applications such as coatings on stainless steel as bipolar plates [9, 10], barrier layer [11], protective coatings for cutting tools, hard coatings for automotive industry, coatings in the biomedicine industry [12] and in tribological applications [13] and so on. The research in the last years regarding the nitride coatings are proposing the use of some nitride films (e.g. titanium nitride) as diffusion barriers in the microelectronics industry or for manufacturing microelectromechanical systems (MEMS).

Chromium nitride thin films are characterized principally by high hardness, high electrical and thermal conductivities, low friction coefficient, good corrosion resistance [9, 12]. This material is stable in two forms namely chromium nitride, CrN, and dichromium nitride, Cr_2N. These two forms are characterized by different properties (tribological, physical etc.) [14]. These types of coatings can be deposited by different methods such as arc ion plating [10, 15], unfiltered cathodic arc evaporation [16], ion beam assisted deposition [17, 18], unbalanced magnetron sputtering [11, 13, 19], RF (radio frequency) or DC (direct current) magnetron sputtering [20–23] and all that.

The obtaining of one of the two forms (CrN or Cr_2N) is strongly influence by the deposition parameters. For instance, in the case of DC magnetron sputtering, the deposition can be done at different parameters such as different temperatures, nitrogen flows, pressures, deposition times, biases etc. The nitrogen flow plays an important role in depositing chromium nitride thin films – this ensures the obtaining of materials main structure.

This research is a study on chromium nitride thin films deposited by direct current reactive magnetron sputtering (DCRMS) on silicon substrates at different parameters such as nitrogen flow, pressure and substrate temperatures. The atomic force microscopy investigations and the X-ray diffraction analyses aim at highlighting the influence of the parameters mentioned before on the topographical, tribological and mechanical properties.

2. MATERIAL AND METHODS

Chromium nitride thin films were deposited by DC reactive magnetron sputtering on silicon Si (100) substrates. A chromium target with purity of 99.95% was employed to deposit the coatings. The atmosphere inside the chamber was formed by a mixture of argon and nitrogen. First the silicon substrates were cleaned in an ultrasonic bath with isopropyl alcohol to remove any possible impurities. After that the substrates were blown with compressed air.

The depositions were realized in high vacuum (10^{-7} torr) which was obtained using a Varian TV551 turbo-molecular pump. The discharge current and the argon flow were kept constant at 500 mA and 40 $cm^3 \cdot min^{-1}$ respectively. The films were deposited for 10 minutes. The distance between the target and the substrates was 60 mm. The depositions of chromium nitride thin films were done at different nitrogen flows, pressures and substrate temperatures. Some films were deposited on silicon substrates at room temperature and the rest were deposited on silicon substrates preheated at 200°C. An increase of the substrate temperature up to about 60°C was also notice for the coatings deposited at room temperature due to the contact with the plasma. Three different pressures were used namely $266 \cdot 10^{-3}$, $279 \cdot 10^{-3}$ and $293 \cdot 10^{-3}$ Pa respectively to highlight its influence on the characteristics of the deposited films. The depositions were carried out at nitrogen flows of 2, 4 and 6 $cm^3 \cdot min^{-1}$.

In order to facilitate the interpretation of the results, the following notations were employed: "CrN" + substrate temperature + nitrogen flow + pressure (given in mtorr in order to shorten the coding), where CrN is chromium nitride (e.g. CrN_rt_2_2.2). The codifications and the parameters at which the films were deposited are given in Table 1.

Table 1

The codification and the deposition parameters for the obtained chromium nitride thin films

Sample codification	**Nitrogen flow [$cm^3 \cdot min^{-1}$]**	**Pressure [10^{-3} Pa]**	**Substrate temperature [°C]**
CrN_rt_2_2.2	2	266	RT*
CrN_200_2_2.1	2	279	200
CrN_200_2_2	2	293	200
CrN_rt_4_2.2	4	293	RT
CrN_200_4_2.2	4	293	200
CrN_rt_6_2.2	6	293	RT
CrN_200_6_2.2	6	293	200

* RT stands for room temperature

The deposited coatings were characterized from the topographical, mechanical and tribological point of view at nanoscale by atomic force microscopy investigations. The tests were performed on a XE 70 atomic force microscope (AFM). The relative humidity was 13%, while the temperature was 20°C. The topography, the adhesion and the attractive forces as well as the tribological properties were determined using a NSC35C cantilever. As the manufacturer indicated, the characteristics of this cantilever are: length of 130 μm, width of 35 μm, thickness of 2 μm, force constant of 5.4 $N \cdot m^{-1}$ and resonance frequency of 150 kHz. The determination of the mechanical properties was achieved using a TD 21562 nanoindentor. According to the manufacturer, the characteristics of this nanoindentor are: cantilever stiffness of 144 $N \cdot m^{-1}$, tip radius smaller than 25 nm, tip height of 109 μm, tip thickness of 24 μm and cantilever length of 782 μm respectively. The obtained data were interpreted using the XEI Image Processing Tool for SPM (Scanning Probe Microscopy) data. The films were also characterized from the structural point of view by X-ray diffraction analyses which were performed on an Inel Equinox 3000 Diffractometer. A cobalt Kα radiation with the wavelength of $\lambda = 1.7903$ Å was used while the 2θ angle was varied between 40 and 100°.

3. THEORY

The determination of the friction force between the AFM tip and the deposited chromium nitride coatings was accomplished using the following formula [24, 25]:

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

where F_f represents the friction force, d_z is the deflection of the tip, r is a constant ($r = 0.33$), G is cantilever's shear modulus (for silicon: $G = 50.9 \cdot 10^{-3}$ N·μm^{-2} [26]), s is tip height (s = 15 μm) and h, b and l are the dimensions of the cantilever. These dimensions are given in the previous section (Material and methods).

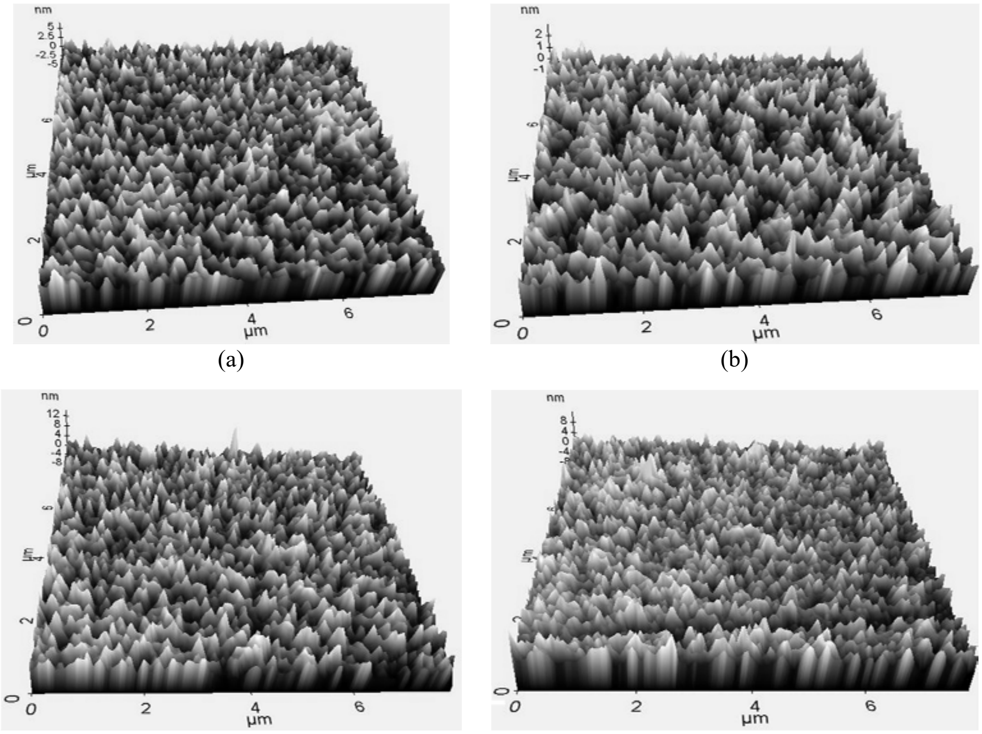
4. RESULTS AND DISCUSSION

The deposited chromium nitride thin films were characterized by topographical, tribological and mechanical point of views at nanoscale determining parameters such as average roughness, friction force, adhesion force, hardness and so on. The nanocharacterization of such coatings is very important in applications in microelectronics and MEMS or NEMS (nanoelectromechanical systems) devices. The change in values of these parameters was explained after performing XRD analyses.

• ***Topography.*** Previous research highlighted the importance of controlling and determining the topography of thin films so that to obtain a good functionality [2007]. This characterization allowed the achieving of 3D images and the determination of the roughness parameters for the tested coatings. 3D images of the chromium nitride thin films deposited at room temperature and at 200°C and at nitrogen flows of 4 and 6 cm^3·min^{-1} are shown in Fig. 1. Once we analyzed these images, we concluded that the deposition of the films on silicon substrates at 200°C results in smoother surfaces than in the case of the films deposited at room temperature regardless of the used nitrogen flows and pressures.

The values of the main topographical parameters are given in Table 2. These parameters are the room mean square, R_q, the average roughness, R_a, the skewness roughness (an asymmetry indicator), R_{sk}, and the kurtosis roughness (an indicator of the shape of the distribution's tails), R_{ku}. The average roughness varied between 1.128 and 1.903 nm, the values of this parameters being influenced by the employed deposition temperature, the nitrogen flow and the pressure.

Concerning pressure influence, when depositing the films at the same nitrogen flow (2 $\mathrm{cm}^3\cdot\mathrm{min}^{-1}$), the average roughness decreased with 32% when the pressure was increased from $266 \cdot 10^{-3}$ to $293 \cdot 10^{-3}$ Pa. When the coatings were deposited at room temperature and the pressure was $293 \cdot 10^{-3}$ Pa, the increase of the nitrogen flow from 2 to 6 $\mathrm{cm}^3\cdot\mathrm{min}^{-1}$ determined an increase of the roughness parameter with about 61% (from 1.179 to 1.903 nm). In the case of the films deposited at 200ºC and at a pressure of $293 \cdot 10^{-3}$ Pa, the increase in average roughness was about 49% when increasing the nitrogen flow from 4 to 6 $\mathrm{cm}^3\cdot\mathrm{min}^{-1}$. In the case of nitrogen flows of 4 and 6 $\mathrm{cm}^3\cdot\mathrm{min}^{-1}$, increasing the substrate temperature from room temperature up to 200ºC led to the decrease of topographical roughness with 29 and 12% respectively. The smallest value of the average roughness was determined on the chromium nitride thin films deposited on silicon substrates at 200ºC using a pressure of $293 \cdot 10^{-3}$ Pa and a nitrogen flow of 4 $\mathrm{cm}^3\cdot\mathrm{min}^{-1}$.



(a) (b)

(c) (d)

Fig. 1 – 3D images of (a) CrN_rt_4_2.2, (b) CrN_200_4_2.2, (c) CrN_rt_6_2.2 and (d) CrN_200_6_2.2 chromium nitride thin films.

Table 2

The roughness parameters of the deposited chromium nitride thin films

Sample codification	R_q [nm]	R_a [nm]	R_{sk} [–]	R_{ku} [–]
CrN_rt_2_2.2	1.444	1.179	–0.214	2.808
CrN_200_2_2.1	2.279	1.759	–0.468	3.742
CrN_200_2_2	2.272	1.745	–0.947	4.330
CrN_rt_4_2.2	2.015	1.579	–0.291	3.430
CrN_200_4_2.2	1.429	1.128	–0.065	3.023
CrN_rt_6_2.2	2.386	1.903	–0.051	3.094
CrN_200_6_2.2	2.086	1.676	–0.173	2.794

• ***Adhesion and attractive forces.*** The reliability of MEMS is strongly influenced by the adhesion, which is one of the major failure mechanisms in this case. The experimental investigation carried out in this respect allowed the determination of the adhesion and attractive forces between the deposited films and the AFM tip as well as the determination of the adhesion energy. The values obtained for the parameters mentioned before are given in Table 3. The adhesion force varied between 59.51 and 136.84 nN. The films deposited on silicon substrates at 200°C for a nitrogen flow of 2 $cm^3 \cdot min^{-1}$ and pressure of $266 \cdot 10^{-3}$ and $293 \cdot 10^{-3}$ Pa are characterized by the smallest values of the adhesion forces. The increase in nitrogen flow resulted in an increase of the adhesion parameter. Except for the coatings deposited at a nitrogen flow of 6 $cm^3 \cdot min^{-1}$, the increase of the substrate temperature from room temperature to 200ºC determined the decrease of this parameters with 25 to 53%. Instead the attractive force varied between 9.70 and 25.40 nN. Increasing the substrate temperature up to 200°C always caused the increase in attractive force. The most significant increase was marked out when the deposition was done at 6 $cm^3 \cdot min^{-1}$ when the attractive force almost doubled its values (from 11.14 to 21.84 nN).

Table 3

The roughness parameters of the deposited chromium nitride thin films

Sample codification	**Adhesion force [nN]**	**Attractive force [nN]**	**Adhesion energy [10^{-15} J]**
CrN_rt_2_2.2	136.84	18.37	4.05
CrN_200_2_2.1	64.65	25.40	1.53
CrN_200_2_2	59.51	19.90	1.49
CrN_rt_4_2.2	93.83	9.70	2.08
CrN_200_4_2.2	70.85	14.16	1.33
CrN_rt_6_2.2	77.73	11.14	1.27
CrN_200_6_2.2	107.04	21.84	2.49

Concerning the adhesion energy, the smallest values were obtained for the films deposited at room temperature for a nitrogen flow of 6 $cm^3 \cdot min^{-1}$ and a pressure of

$293 \cdot 10^{-3}$ Pa ($1.27 \cdot 10^{-15}$ J) while the highest values were marked out on the films deposited at room temperature for a nitrogen flow of 2 $cm^3 \cdot min^{-1}$ and a pressure of $293 \cdot 10^{-3}$ Pa ($4.05 \cdot 10^{-15}$ J). The adhesion energy presented a similar variation as the adhesion force regarding the influence of substrate temperature.

• ***Tribological characterization.*** The characterization of the deposited chromium nitride thin films from the tribological point of view implied the determination of the friction force between the deposited films and the AFM tip. This parameter was calculated according to the formula presented in Section 3 (Theory). The influence of pressure and the influence of nitrogen flow and substrate temperature on the friction force are graphically presented in Fig. 2 and Fig. 3 respectively. A decrease of about 2.7 times (from 8.23 to 3.08 nN) was first determined when increasing the pressure from $266 \cdot 10^{-3}$ to $293 \cdot 10^{-3}$ Pa. A further increase of the pressure to $293 \cdot 10^{-3}$ Pa caused instead an increase of the friction force to 5.76 nN. As seen in Fig. 2, the values obtained for the friction force when using a pressure of $293 \cdot 10^{-3}$ Pa are more stable that those obtained for pressures of $266 \cdot 10^{-3}$ and $279 \cdot 10^{-3}$ Pa.

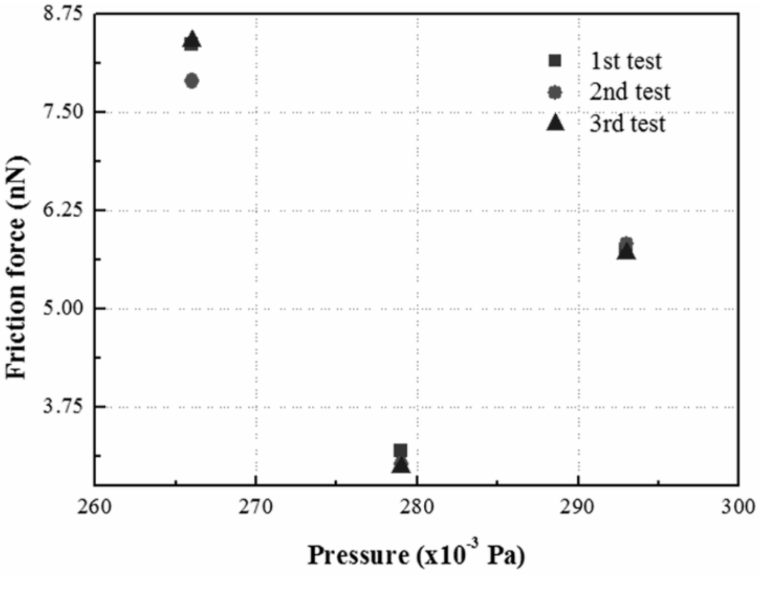


Fig. 2 – Pressure influence on the friction force of the deposited chromium nitride coatings.

The friction parameter decreased when the substrate temperature was increased at 200°C whatever the nitrogen flow was used (Fig. 3). This decrease was most obvious when the nitrogen flow was of 2 and 4 $cm^3 \cdot min^{-1}$. When the films were deposited at room temperature, the increase of the nitrogen flow from 2 to 4 $cm^3 \cdot min^{-1}$ led to a decrease of the friction force with more than 10%. A further increase of nitrogen flow to 6 $cm^3 \cdot min^{-1}$ did not determine a change in this parameter.

Instead when the films were deposited at 200°C, the friction force decreased first when increasing the nitrogen flow from 2 to 4 $cm^3 \cdot min^{-1}$ and increased later when increasing the nitrogen flow from 4 to 6 $cm^3 \cdot min^{-1}$. As seen in Fig. 3, the increase of the friction force from 4 to 6 $cm^3 \cdot min^{-1}$ is more prominent that the decrease from 2 to 4 $cm^3 \cdot min^{-1}$.

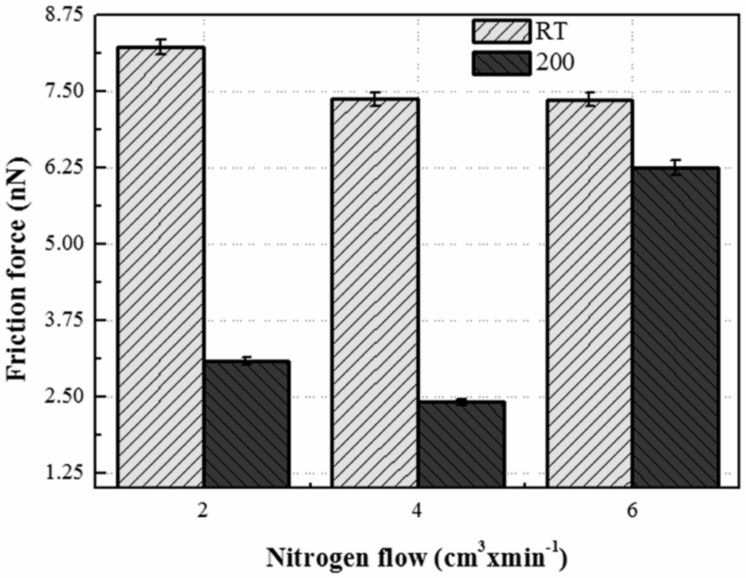


Fig. 3 – The fluctuation of friction force dependent on the nitrogen flow for the tested films.

• ***Mechanical characterization.*** The modulus of elasticity and the nanohardness of the deposited chromium nitride thin films were determined to characterize them from the mechanical point of view. These values were obtained after interpreting the force vs. Z scan curves achieved during the nanoindentation tests. These curves were interpreted using the Oliver and Pharr model for determining the nanohardness and the Hertzian model for determining the modulus of elasticity. The main difference between these two models is the fact that the second model (Hertzian) consider that there is no plastic deformation between the films and the AFM tip.

– **Modulus of elasticity.** Figure 4 presents the variation of the modulus of elasticity (Young's modulus) in terms of pressure. At the first glance, we can notice that the values of this mechanical characteristic are more stable than those determined for the friction force, a slight variation being observed in the case of the films deposited at a pressure of $293 \cdot 10^{-3}$ Pa. The increase of the pressure from $266 \cdot 10^{-3}$ to $293 \cdot 10^{-3}$ Pa caused a continuous decrease of the modulus of elasticity with about 39%. The average values of Young's modulus varied between 18.47 (when depositing at a pressure of $293 \cdot 10^{-3}$ Pa) and 30.15 GPa (when depositing at $266 \cdot 10^{-3}$ Pa).

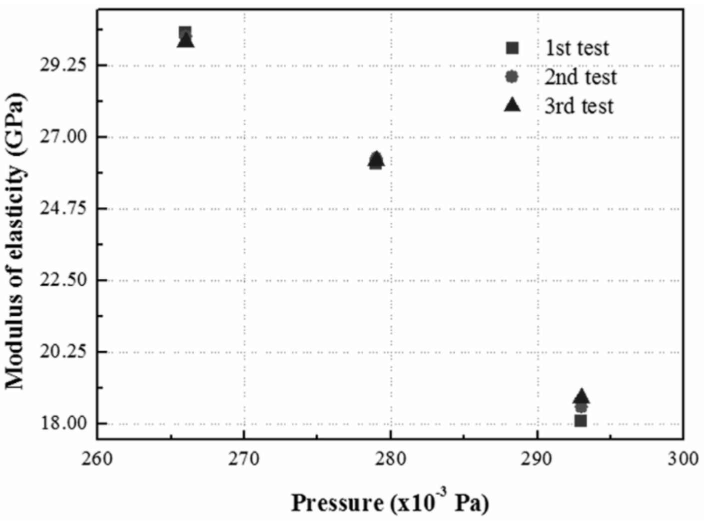


Fig. 4 – The influence of the pressure on the modulus of elasticity of the deposited chromium nitride thin films.

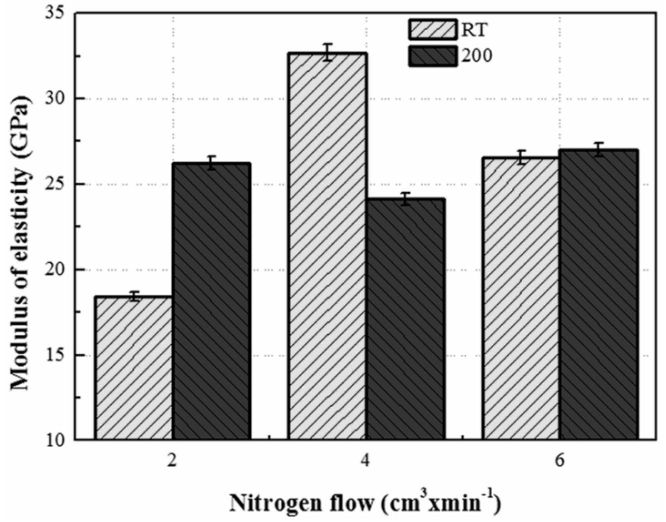


Fig. 5 – The fluctuation of modulus of elasticity in terms of nitrogen flow for the testing coatings.

The fluctuation of the modulus of elasticity dependent on the nitrogen flow and substrate temperature is given in Fig. 5. An irregular variation can be observed when analyzing both the nitrogen flow and substrate temperature influence. When we kept constant the nitrogen flow, increasing the substrate temperature determined a significant increase of modulus of elasticity only in the case of the films deposited at a nitrogen flow of 2 $cm^3 \cdot min^{-1}$. These films present a higher Young modulus with about 42%. A slight increase was also noticed for the films deposited at a nitrogen flow of 6 $cm^3 \cdot min^{-1}$ (from 26.55 to 27.01 GPa). Instead the deposition at a nitrogen flow of 4 $cm^3 \cdot min^{-1}$ caused an important decrease of modulus of elasticity with about 26% when increasing the substrate temperature. When the substrate temperature was the room temperature, the increase of nitrogen flow from 2 to 4 $cm^3 \cdot min^{-1}$ led to an increase with 77% of these properties followed by a decrease of about 19% when the nitrogen flow was increased to 6 $cm^3 \cdot min^{-1}$. When the films were deposited at 200°C, a slight variation can be marked out, the average values of the modulus of elasticity being of 26.25, 24.13 and 27.01 GPa when the nitrogen flow was of 2, 4 and 6 $cm^3 \cdot min^{-1}$ respectively.

– **Nanohardness.** As compared to the modulus of elasticity, the nanohardness presents a different variation in terms of pressure as can be seen in Fig. 6. If the Young's modulus decreased with increasing the pressure, the nanohardness recorded a slight increase when increasing the pressure from $266 \cdot 10^{-3}$ to $279 \cdot 10^{-3}$ Pa followed by a more pronounced decrease when increasing the pressure from $279 \cdot 10^{-3}$ to $293 \cdot 10^{-3}$ Pa. We should note that the values obtained for this parameter are the most stable than those determined for the friction force and the modulus of elasticity. The values of nanohardness varied between 0.94 GPa specific to the films deposited for a pressure of $293 \cdot 10^{-3}$ Pa and 1.42 GPa specific to the films deposited at a pressure of $279 \cdot 10^{-3}$ Pa.

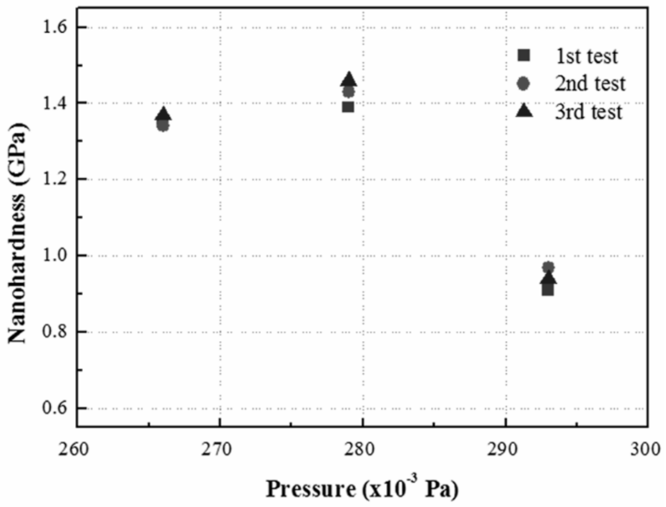


Fig. 6 – The influence of the pressure on the nanohardness of the deposited chromium nitride thin films.

Concerning the influence of nitrogen flow and substrate temperature, the variation of nanohardness dependent on these deposition parameters is given in

Fig. 7. Two different trends were observed when analyzing the influence of substrate temperature. The first trend is specific to the samples deposited at room temperature when the increase of nitrogen flow from 2 to 6 cm^3·min^{-1} led to the increase of nanohardness with about 64% (from 0.94 to 1.54 GPa) and the second specific to the samples deposited at 200°C when the increase of nitrogen flow from 2 to 6 cm^3·min^{-1} determined the decrease of nanohardness with about 30% (from 1.42 to 0.99 GPa). An increase with more than 50% was highlighted along with the increase of substrate temperature when depositing the films at a nitrogen flow of 2 cm^3·min^{-1}. Instead in the case of the films deposited at 4 and 6 cm^3·min^{-1}, the increase in substrate temperature resulted in a decrease of this mechanical characteristic. This decrease was more pronounced on the films deposited at a nitrogen flow of 6 cm^3·min^{-1} when the nanohardness decreased from 1.54 (specific to the films deposited at room temperature) to 0.99 GPa (specific to the films deposited at 200°C).

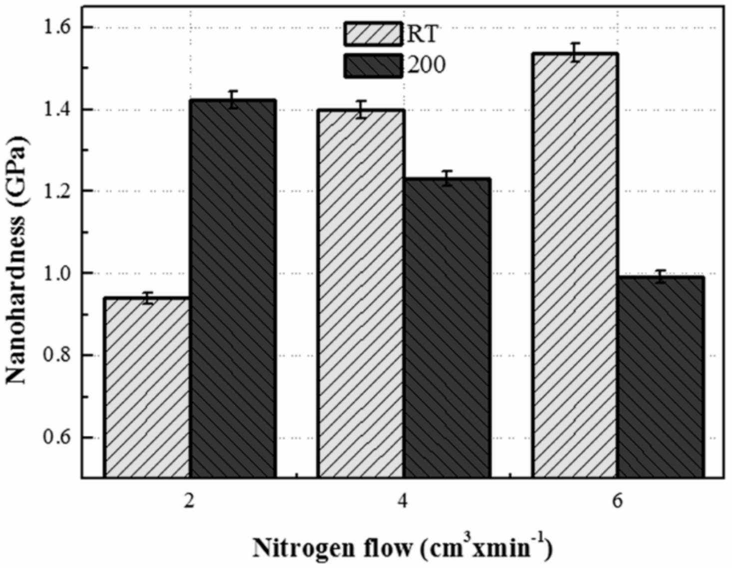


Fig. 7 – The fluctuation of nanohardness according to the nitrogen flow for the tested coatings.

The results obtained for both the hardness and modulus of elasticity for the investigated chromium nitride thin films are comparable to those presented in the scientific literature [21, 27, 28].

The nanohardness/modulus of elasticity ratio (*H*/*E*) was determined to establish the films characterized by the best mechanical behavior. The values calculated are presented in Table 4. It can be concluded that the highest values for this ratio is specific to the chromium nitride tin films deposited at room temperature, for a pressure of 293 · 10^{-3} Pa and a nitrogen flow of 6 cm^3·min^{-1}. It seems that the improvement in mechanical properties is due to films growth by multiple preferential orientations.

Table 4

The nanohardness/modulus of elasticity of the deposited thin films

Sample codification	*H*/*E* ratio [–]
CrN_rt_2_2.2	0.051
CrN_200_2_2.1	0.054
CrN_200_2_2	0.045
CrN_rt_4_2.2	0.043
CrN_200_4_2.2	0.051
CrN_rt_6_2.2	0.058
CrN_200_6_2.2	0.037

• ***XRD analyses.*** X-ray diffraction (XRD) analyses were performed in order to characterize the films from the structural point of view. The XRD patterns obtained for the films deposited at a nitrogen flow of 2 $cm^3 \cdot min^{-1}$ highlighted a growth of these films mainly after the (200) preferential orientation. An example of such a pattern is given in Fig. 8, pattern that is characteristic to the CrN_rt_2_2.2 film.

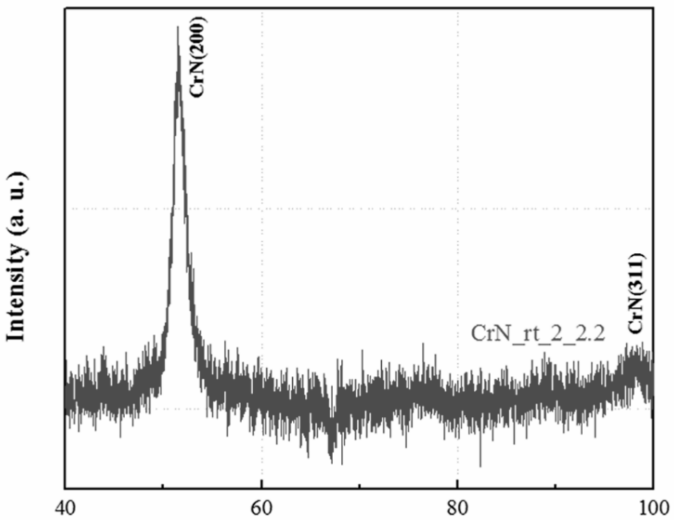
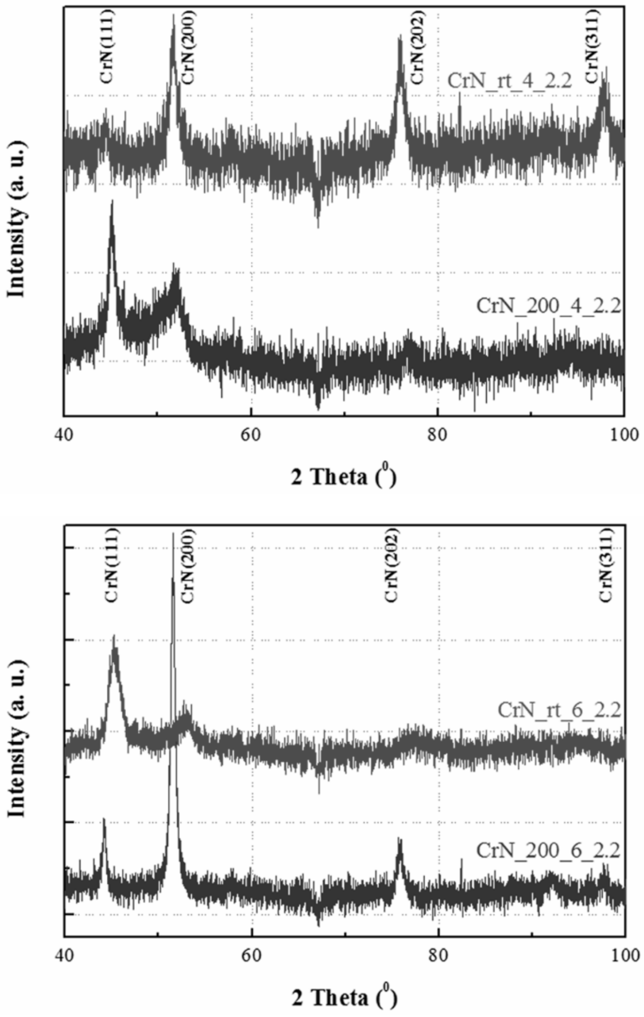


Fig. 8 – XRD pattern of the CrN_rt_2_2.2 chromium nitride thin films.

Instead the XRD patterns achieved for the chromium nitride thin films deposited at 4 (Fig. 9a) and 6 (Fig. 9b) $cm^3 \cdot min^{-1}$ marked out the fact that the growth of the coatings was done after multiple preferential orientations. Two, three or four peaks namely (200), (111), (202) and (311) can be observed on these patterns. In the case of the film deposited at a nitrogen flow of 4 $cm^3 \cdot min^{-1}$, the intensity of the (200) peak decreased at the same time the intensity of (111) peak increased strongly when increasing the substrate temperature to 200°C. The same increase in substrate temperature resulted in the decrease of the intensity of the (202) and (311) peaks. Instead the XRD patterns for the coatings deposited at a nitrogen flow of 6 $cm^3 \cdot min^{-1}$ denotes a strong increase in intensity of the (200) peak along with a decrease of the intensity of (111) peak.



(a)

(b)

Fig. 9 – XRD pattern of the chromium nitride thin films deposited at room temperature and 200°C and at a nitrogen flow of (a) 4 $cm^3 \cdot min^{-1}$ and (b) 6 $cm^3 \cdot min^{-1}$.

5. CONCLUSIONS

Chromium nitride thin films were deposited on silicon substrates by direct current reactive magnetron sputtering at different substrate temperatures, pressures and different nitrogen flows. The atomic force microscopy investigations performed highlighted a significant impact of both nitrogen flow and substrate temperature on the topographical parameters. The adhesion force was most strongly influenced by the pressure inside the deposition chamber, the highest value being determined when the pressure was $293 \cdot 10^{-3}$ Pa. The heating of the substrate at 200°C had a major influence on the friction force which was reduced three times in some cases. The mechanical properties – both the modulus of elasticity and the nanohardness – were irregular changed by the modification of the deposition parameters. The chromium nitride coatings characterized by the best mechanical behavior were deposited at a nitrogen flow of 6 $\text{cm}^3 \cdot \text{min}^{-1}$ when depositing at room temperature. The change in thin films properties is attributed to the different preferential growth of the deposited coatings, which was marked out by the X-ray diffraction analyses.

Acknowledgements. This paper is written within the TUCN Internal Research Project Competition 2015 “Elaboration and structural, tribo-mechanical and optical characterization of some nitride thin films for MEMS applications (NitriMEMS)” (C.I.5/1.2/2015). The Internal Research Project Competition is funded by the Technical University of Cluj-Napoca in order to support and encourage young teams in addressing new topics in priority research areas of the university.

Received on December 5, 2018

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