Temperature influence on mechanical properties of chromium nitride thin films

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Abstract. Thin films present interest for researchers due to their applicability in areas such as developing microelecromechanical devices, hard coatings, cutting tools and diffusion barriers. This paper is focused on studying the influence of the testing temperature on the mechanical properties of chromium nitride (CrN) thin films. For this purpose, CrN thin films were deposited by direct current magnetron sputtering on silicon substrate using a chromium target of high purity. All the films were obtained by keeping almost all deposition parameters constant, while the nitrogen flow rate was varied. Hence, three types of samples of CrN thin films were obtained using different nitrogen flow rates namely 2 cm^3/min, 4 cm^3/min and 6 cm^3/min. The mechanical properties of these thin films such as the hardness and Young's modulus were investigated by performing nanoindentation using an atomic force microscope. All experimental investigations were conducted by varying the testing temperature between 20 ºC and 100 ºC. The purpose was to find the dependency between the testing temperature and the mechanical properties of CrN films deposited at different nitrogen flow rates. The obtained experimental results indicate a significant influence of the testing temperature on the properties of the studied CrN thin films.

1. Introduction

Thin films industry has presented interest both to researchers and companies due to the many real-world applications that require thin films. In particular, CrN thin films can be used in different applications due to their good corrosion and oxidation features [1]. Several studies have been conducted on CrN thin films with respect to the deposition procedure which can vary from direct current (DC) or radio-frequency (RF) magnetron sputtering [2] to vacuum arc plasma deposition [3] or ion beam assisted deposition [4]. The main purpose of such studies was to characterize the thin films using different techniques ([1, 5-8]) or to determine the influence of the deposition parameters on the film structure [9] or the adhesion force [10]. Nevertheless, there aren't studies available in the open literature that target the influence of the deposition parameters on the mechanical properties of CrN thin films determined using the atomic force microscopy (AFM).

The AFM has been used as a complementary method to other techniques with the purpose of ensuring a more complete characterization of the CrN thin film samples. Relevant examples encompass the experiments conducted by X-ray diffraction and scanning electron microscopy [11], by X-ray photoelectron spectroscopy [12] or by transmission electron microscopy and glow-discharge optical emission spectroscopy [13].

The purpose of this work is to deposit the CrN thin films by DC reactive magnetron sputtering using different nitrogen flow rates and to characterize them using the nanoindentation module of the AFM at different testing temperatures. The obtained experimental results will allow to identify the temperature effect on the deposited samples, as well as to determine the thin films characterized by the best mechanical behavior.

2. Materials and experimental procedure

The samples of CrN thin films were deposited on silicon Si (100) substrates. The deposition process employed a chromium target with a purity of 99.95 % and was conducted by DC magnetron sputtering. The deposition chamber atmosphere contained a mixture of argon and nitrogen. The nitrogen flow rate varied for each sample as it can be seen in table 1, while the argon flow rate was kept constant at 40 $cm^3 \cdot min^{-1}$. All other deposition paraments were also kept constant.

The experimental investigations on the deposited CrN thin films were conducted using a XE 70 AFM at the Micro and Nano Systems Laboratory, from the Technical University of Cluj-Napoca. First all samples were scanned in the non-contact mode of the microscope using a PPP-NCHR cantilever in order to determine the topography of each sample. Then, using the nanoindentation module of the AFM the mechanical properties of the samples were experimentally determined at different temperatures namely 20, 40, 60, 80 and 100 ℃ respectively. The tests were performed at a relative humidity of 20 %.

Table 1. Deposition conditions for investigated samples.

Sample	T (°C)	Time (min)	P (mtorr)	Id (mA)	Q_{Ar} (cm³/min)	Q_{N2} (cm³/min)
CrN_2						2
CrN_4	200	20	2.2	300	40	4
CrN_6						6

3. Results and discussions

3.1 Topography

After the deposition of the samples of CrN thin films, they were characterized using the AFM. First, the topography was investigated. Each sample was scanned in non-contact mode and, using the XEI Image Processing Tools for SPM data, 3D images such as the one in figure 1 were obtained.
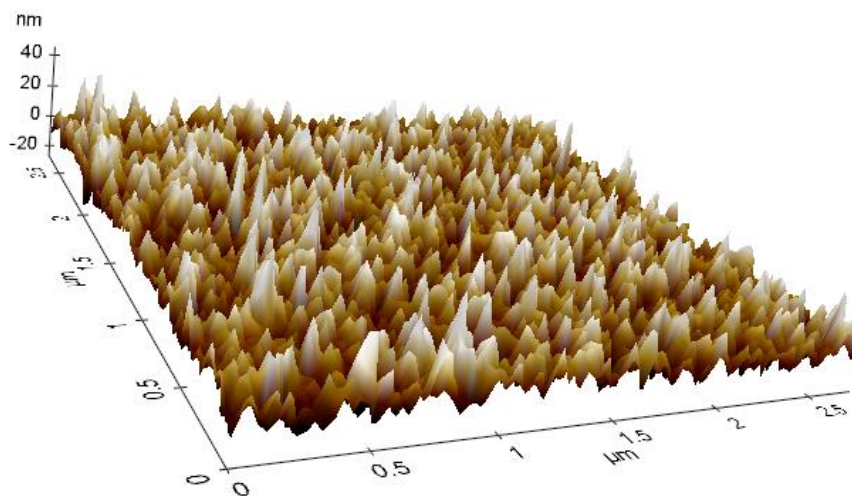

Figure 1. The 3D image of the sample CrN_6.

Also, the software provided statistical roughness parameters for each thin film such as the ones presented in figure 2. The values of the average roughness, R_a, the average maximum height of the profile, R_z, the skewness of the roughness, R_{sk}, and the kurtosis of the roughness, R_{ku}, determined at a testing temperature of 20 ºC for all samples are encompassed in table 2. As it can be observed, the sample deposited at the smallest nitrogen flow rate has the smallest average roughness. The increase in the nitrogen flow rate up to 4 cm³/min determines an increase in this roughness parameter up to 2.8 nm. However, a more significant increase in the average roughness is recorded when the nitrogen flow rate was further increased to 6 cm³/min.
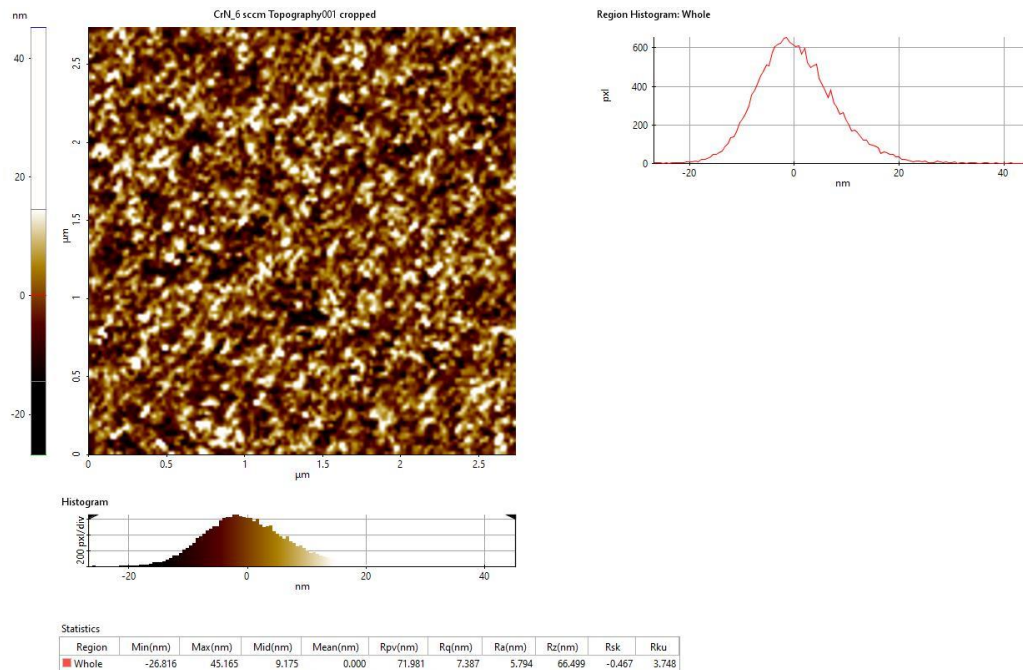

Figure 2. The surface of the sample CrN_6 and the statistical parameters provided for its roughness by the AFM software.

Table 2. Statistical roughness parameters for all samples.

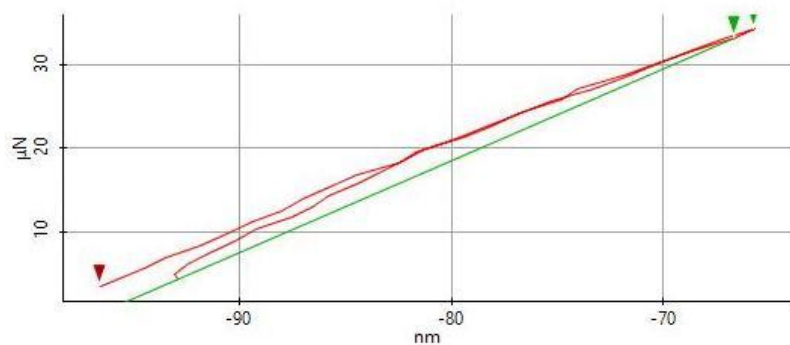| Parameter \ Sample	CrN_2	CrN_4	CrN_6
R_a (nm)	1.1	2.8	5.8
R_z (nm)	15.0	30.5	66.5
R_{sk} (-)	0.4	-1.2	-0.5
R_{ku} (-)	4.7	5.3	3.7

3.2 Nanohardness and Young's modulus

In order to characterize the samples from the mechanical point of view, nanoindentation tests were performed. After these tests, force vs. Z scan curves similar to the one presented in figure 3 were obtained. These curves were interpreted using the Oliver and Pharr method in order to determine the nanohardness of the thin films and the Hertzian model in order to determine Young's modulus.

Figure 4 presents the variation of the nanohardness for all samples with respect to the testing temperature. It can be seen that this mechanical characteristic increased with the increase in nitrogen flow rate when tested at 20 °C, 80 °C and 100 °C. For the other two testing temperatures the largest

values for the nanohardness have been obtained for the CrN_4 sample, while for all temperatures the lowest values for the nanohardness were obtained for the CrN_2 sample. When analyzing the results for each sample with respect to the variation of the testing temperature, it can be observed that the nanohardness values decrease for all samples. First, the decreasing trends are steep, then they become mild and in the end the decrease in the values of the nanohardness becomes strong again for all samples. The largest total decrease of almost 76% was registered for the CrN_2 sample, while the lowest of almost 66% was registered for the CrN_6 sample.

Figure 3. Image of the XEI Image Processing Tools for SPM Data for determining the hardness of the sample CrN_6 and tested at 20 °C.

Decreasing trends with respect to the increase in the testing temperature were obtained for all samples when analyzing the experimental results for the modulus of elasticity. There is an almost linear decreasing trend for the CrN_2 sample, with a step of almost 9% decrease with every increase of 20 ºC in the testing temperature. For the CrN_4 sample the largest decrease is around 15% and it is observed when increasing the temperature from 80 to 100 ºC. For the CrN_6 sample the largest decrease in the values of Young's modulus is around 17% and it is observed when increasing the temperature from 20 to 40 ºC. The total decrease in the values of the modulus of elasticity was lower for each sample when compared to the decrease registered for the values of the nanohardness. The largest total decrease of around 37% was registered for the CrN_6 sample, while the lowest of around 30% was registered for the CrN_4 sample. The change that occurs in the values of the mechanical properties is due to the growth after different preferential directions. Hence, the values of the studied mechanical properties may fluctuate depending on the main growth direction.

To identify the thin film with the best mechanical behavior, the nanohardness/modulus of elasticity ratio was computed. For each of the three types of thin films the ratio was computed for all testing

temperatures and the results are presented in table 3. As it can be observed the ratio decreases for the first two samples with the increase in testing temperature. For the third sample the exception from the decreasing the trend is due to the ratio of the mechanical properties obtained when the tests were performed at 40 ºC. For the same testing temperature, the increase in nitrogen flow rate determines an increase in the studied ratio for the tests performed at 80 and 100 ºC. This increase is rather significant at 80 ºC when the ratio doubles its value. For the tests performed at 20, 40 and 60 ºC the largest values of the ratio are obtained for the CrN_4 sample, while the lowest for the CrN_2 sample. The chromium nitride thin film deposited at a nitrogen flow rate of 4 $cm^3 \cdot min^{-1}$ and tested at 20 ºC has the highest value of the ratio between the nanohardness and the modulus of elasticity and therefore, the best mechanical behavior for applications such as hard coatings.
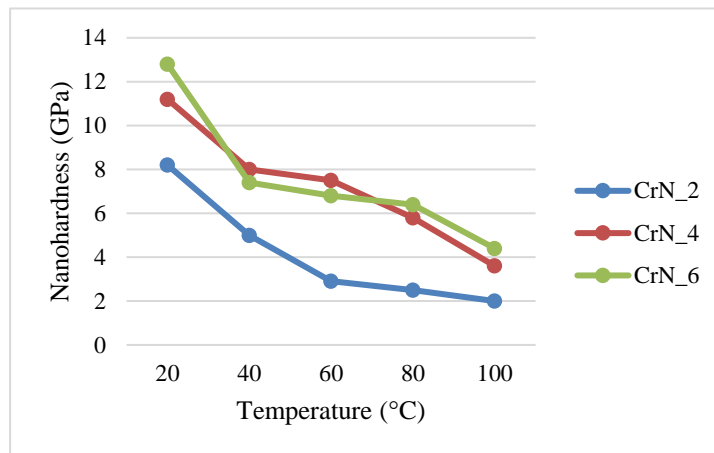

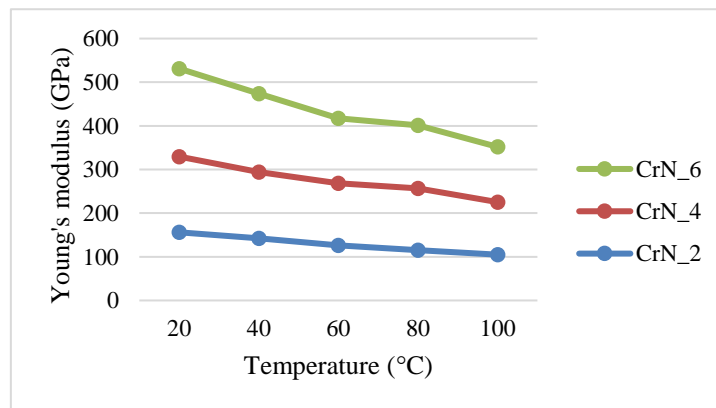**Figure 4.** Nanohardness variation with respect to testing temperature.

Figure 5. Young's modulus variation with respect to testing temperature.

Table 3. Nanohardness/Young's modulus of the investigated samples.

Sample	Nanohardness/Young's modulus, H/E (-)				
	20 °C	40 °C	60 °C	80 °C	100 °C
CrN_2	0.053	0.035	0.023	0.022	0.019
CrN_4	0.065	0.053	0.053	0.041	0.030
CrN_6	0.063	0.041	0.046	0.044	0.035

4. Conclusions

This paper presents the deposition by DC magnetron sputtering of three sets of samples of CrN thin films using different nitrogen flow rates. The deposited thin films were characterized from the topographical and mechanical point of view using the AFM. An increasing trend of the roughness was observed with respect to the increase of the nitrogen flow rate. Moreover, an increasing trend was observed for the modulus of elasticity values with respect to the increase of the nitrogen flow rate regardless of the testing temperature and an increasing trend was identified for the values of the nanohardness only when the tests were performed at 20, 80 and 100 °C.

Also, the work conducted for this paper encompassed the study of the influence of the testing temperature on the mechanical properties of the CrN thin films. Moreover, the ratio between the nanohardness and modulus of elasticity was determined for all samples at all testing temperatures in order to emphasize the sample with the best mechanical behavior, which proved to be the CrN_4 sample.

5. References

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