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Adhesion analysis for chromium nitride thin films deposited by reactive magnetron sputtering

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Abstract. The thin film industry is continuously growing due to the wide range of applications that require the fabrication of advanced components such as sensors, biological implants, micro-electromechanical devices, optical coatings and so on. The selection regarding the deposition materials, as well as the deposition technology influences the properties of the material and determines the suitability of devices for certain real-world applications. This paper is focused on the adhesion force for several chromium nitride thin films obtained by reactive magnetron sputtering. All chromium nitride thin films were deposited on a silicon substrate, the discharge current and the argon flow being kept constant. The main purpose of the paper is to determine the influence of deposition parameters on the adhesion force. Therefore some of the deposition parameters were varied in order to study their effect on the adhesion force. Experimentally, the values of the adhesion force were determined in multiple points for each sample using the spectroscopy in point mode of the atomic force microscope. The obtained values were used to estimate the surface energy of the CrN thin films based on two existing mathematical models for the adhesion force when considering the contact between two bodies.

1. Introduction

An intensification of the interest in adhesion forces in direct connection to thin film industry has been detected in the last decade. This interest has materialized into thorough research and important theoretical and experimental results in the fields of microtribology and nanotribology.

Established methods of measuring the adhesion force consist in using the atomic force microscope (AFM) and the surface forces apparatus (SFA). Due to the fact that the AFM measurements are high-resolution ones and grant access to atomic characteristics [1] are recommended for determining the adhesion forces. The cantilever of the AFM has a tip which is taken into the proximity of sample surface and which is deflected due to the attraction forces that occur between the tip and the sample. The deflections of the cantilever are measured using a laser and a detector [2]. An advantage of using the AFM consists in the fact that it provides not only the surface topography, but also important statistical surface parameters [3].

The AFM has been used together with other microscopes or other techniques in order to provide a more plenary characterization of samples. For example, its measurements have been completed by the

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X-ray photoelectron spectroscopy in order to provide an evaluation of adhesion and nanostructure of thin Cr films [4]. More recently, the trivalent chromium conversion coating formation associated with aluminium dissolution process has been studied using the atomic force microscopy, the transmission electron microscopy, and the glow-discharge optical emission spectroscopy [5].

The chromium nitride thin films have presented interest to researchers due to their good corrosion and oxidation features [6]. Taking into account the deposition procedure they have been characterized using different techniques such as XRD (X-ray diffraction) and DTG (differential thermogravimetric analysis) [7], SEM (scanning electron microscopy) and EDX (energy dispersive X-ray analysis) [6] and even using the AFM [8]. Even the influence of the deposition parameters on the film structure has been studied [9]. However, none of the studies focused on the influence of deposition parameters on the adhesion force determined using the AFM.

The AFM investigations that concern this study are the ones that refer to the minimum force required for the separation between the AFM tip and the sample. That actually gives the adhesion force, also known as the pull-off force. The experimental tests were performed using the spectroscopy in point mode of the AFM and their purpose was to find the adhesion force between the AFM tip and the seven investigated CrN thin films. The main goal was to determine the influence on the adhesion force of the parameters which varied during the deposition procedure. A complementary goal was to determine the surface energy of the CrN samples using existing mathematical models.

2. Materials and experimental procedure

2.1. Materials

The samples investigated for this paper are thin solid films of chromium nitride consisting in one layer of chromium nitride deposited on silicon Si (100) substrate in different conditions by reactive magnetron sputtering using a Cr target with purity of 99.95%. As shown in table 1 the intensity of the discharging current I_d, the argon flow Q_{Ar}, the distance between the target and the substrate $d_{t\text{-}s}$, and the deposition time were kept constant, while the nitrogen flow Q_{N2}, the pressure P, and the temperature T were varied.

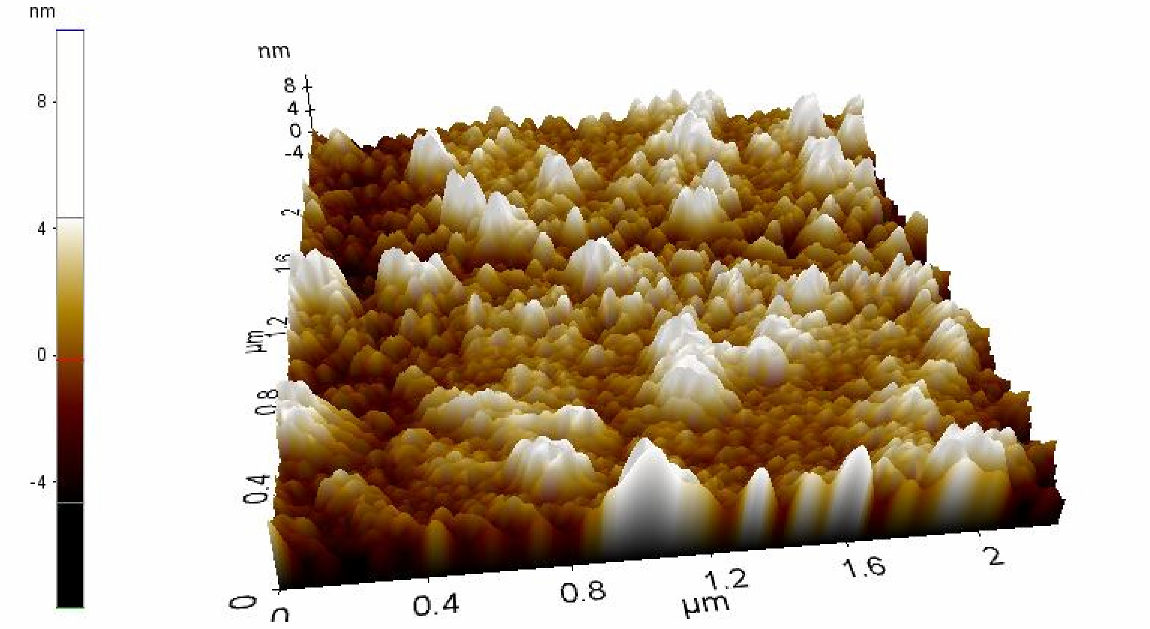
Table 1. Deposition conditions for all investigated samples.

Sample	I_d (mA)	Q_{Ar} (cm^3/min)	Q_{N2} (cm^3/min)	P (mtorr)	$d_{t\text{-}s}$ (mm)	Time (min)	T (°C)
CrN1	500	40	1.0	2.0	60	10	200
CrN2	500	40	2.0	2.1	60	10	200
CrN3	500	40	4.0	2.2	60	10	200
CrN4	500	40	4.0	2.2	60	10	36/64
CrN5	500	40	6.0	2.3	60	10	200
CrN6	500	40	2.0	2.2	60	10	33/62
CrN7	500	40	6.0	2.2	60	10	26/57

The investigations regarding the adhesion force were conducted on the obtained samples due to a large spectrum of applications for chromium nitride thin films.

The used AFM software provides the following main statistic parameters: average roughness R_a, root mean square R_q, skewness R_{sk} (asymmetry indicator), and kurtosis R_{ku} (indicator of the shape of the distribution's tails), parameters which characterize the surface roughness of a sample.

An example of the statistical parameters used for the roughness characterization of each CrN surface of approximately 3 µm x 3 µm are given in figure 1. Similar tables were generated by the AFM software for each of the seven investigated samples. The statistical data is summarized in table 2. As it can be seen the first CrN sample obtained at a temperature of 200 °C, using a nitrogen flow of 1.0 cm^3/min and a pressure of 2.0 mtorr is characterized by the largest roughness, while the third CrN sample obtained at a temperature of 200 °C, using a nitrogen flow of 4.0 cm^3/min and a pressure of 2.2 mtorr has the lowest roughness.



Statistics

Region	Min(nm)	Max(nm)	Mid(nm)	Mean(nm)	Rpv(nm)	Rq(nm)	Ra(nm)	Rz(nm)	Rsk	Rku
Red	-7.968	10.257	1.144	-0.156	18.225	2.301	1.776	16.880	-0.429	3.724

Figure 1. 3D image of the CrN surface of the second sample and the statistical parameters provided for its roughness by the AFM software.

Table 2. Statistical parameters for roughness characterization of all investigated samples.

Parameter	Sample						
	CrN1	CrN2	CrN3	CrN4	CrN5	CrN6	CrN7
R_a (nm)	3.158	1.776	1.077	1.652	1.589	1.155	1.994
R_q (nm)	4.160	2.301	1.361	2.163	1.981	1.409	2.506
R_{sk}	-0.804	-0.429	-0.018	-0.652	-0.089	-0.161	-0.044
R_{ku}	4.180	3.724	3.102	5.442	2.850	2.803	2.923

2.2. Experimental procedure

The characterization of the seven thin films at nano-scale was achieved using a XE 70 AFM in the Micro & Nano Systems Laboratory from the Technical University of Cluj-Napoca. All tests were performed at a relative humidity of 31 %, a temperature of 22 °C and a scanning frequency of 1 Hz. A NSC35C cantilever was used which, according to the manufacturer specifications has a length of 130 µm, a width of 35 µm, a thickness of 2 µm, a force constant of 5.4 N/m and a resonance frequency of

150 kHz. The radius tip of the cantilever is smaller than 20 nm. In order to interpret the obtained data the XEI Image Processing Tool for SPM (Scanning Probe Microscopy) program was used.

Using the spectroscopy in point mode of the AFM the adhesion forces between the tip of the cantilever and the considered CrN thin films were determined. The used method provided AFM experimental curves similar to the one presented in figure 2 which highlight the loading and the unloading phases of the procedure. The values of the adhesion forces between the AFM tip and each of the seven CrN thin films were obtained based on these curves.

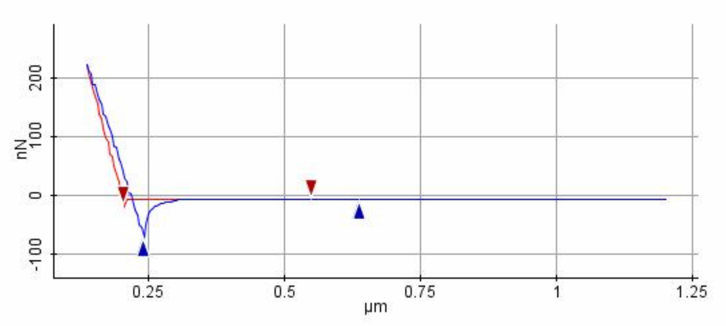


Figure 2. A force vs. z scan curve for the contact between the Si_3N_4 AFM tip and the CrN surface of the second investigated sample.

The measurements of the adhesion force were conducted in multiple points. For each sample a grid of 16 squares was considered (see figure 3) and the adhesion force was determined for the centre of each square.

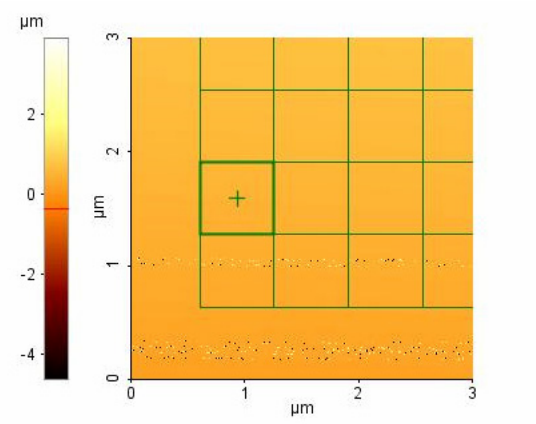


Figure 3. The image of the second CrN thin film obtained with the XEI Image Processing Tool for SPM Data.

3. Theoretical formula

The type of contact between the surfaces influences the adhesion measurements. The modelling of this contact has led to several models that are used to estimate the adhesion force. Two of the most used models are the JKR model and the DMT model, which were developed in order to eliminate the inconsistencies between the experimental vales and the ones obtained based on the Hertz theory when applying low loads. For the JKR model [10], the radius of the circular contact area between a sphere of radius R and a plane is expressed as a function of the surface energy γ :

$$a = \left\{ \frac{R}{K} \left[P + 3\gamma\pi R + \sqrt{6\gamma\pi RP + \left(3\gamma\pi R\right)^2} \right] \right\}^{1/3} \tag{1}$$

where K is a constant depending on Young's module and Posison's ratio corresponding to each surface and P is the applied load.

The surface energy γ is also known as Dupré energy of adhesion [11] or work of adhesion [12, 13, 14]. It is defined as the energy per unit area and it represents the work done to completely separate a unit area of the interface [11]. The adhesion force is given by [10]:

$$F_{ad}^{JKR} = \frac{3}{2}\pi\gamma R \tag{2}$$

Recently, in [15], the authors proposed a generalization of this model by including the surface effect. The other mentioned model, the DMT model, is based on the assumption of a larger load due to adhesion, while maintaining the same contact profile as in the Hertz theory. The radius of the circular contact area between a plane and a sphere of radius R is given by the formula [11]:

$$a = \left[\frac{R}{K}\left(P + 2\pi\gamma R\right)\right]^{1/3} \tag{3}$$

while, the adhesion force force is given by:

$$F_{ad}^{DMT} = 2\pi\gamma R \tag{4}$$

4. Results and discussions

As already mentioned the main purpose of this paper is to determine the influence on the adhesion force of several deposition parameters whose variation was presented in table 1. Consequently, the adhesion force was determined for each sample in multiple points as shown in figure 3. The obtained values are summarized in table 3.

Table 3. Statistics for adhesion force characterization of all investigated samples.

Adhesion force[nN]	Sample						
	CrN1	CrN2	CrN3	CrN4	CrN5	CrN6	CrN7
Minimum value	57.56	64.04	69.28	90.09	105.58	133.42	67.98
Maximum value	64.53	69.93	75.81	114.43	114.20	139.75	93.49
Mean value	61.00	66.20	72.01	100.42	108.91	136.89	80.70
Standard deviation	2.40	2.35	2.60	9.57	3.03	1.98	9.33

As it can be seen the sixth sample has the highest values for the adhesion force and the lowest standard deviation. When comparing it to the second sample it results that using the same nitrogen flow the adhesion force decreases up to almost 52% with the increase of temperature and the decrease of pressure. A smaller decrease of about 28% of the adhesion force average values with respect to the increase of temperature in the presence of constant pressure can be seen when comparing CrN4 to CrN3. However, despite the temperature increase, when the pressure increases the adhesion force also increases (see CrN7 vs. CrN5). When comparing samples CrN1, CrN2, CrN3, and CrN5 obtained at a constant deposition temperature, it can be seen that the increase of nitrogen flow and pressure determines an increase of the adhesion force. If comparing the other samples obtained at ambient temperature and constant pressure of 2,2 mtorr, it results that the adhesion force decreases with the increase of nitrogen flow.

A subsidiary goal of this paper is to determine the surface energy of the investigated CrN thin films. As it can be seen in table 2 they have low roughness values, and therefore, the contact between the thin films and the AFM tip can be modelled as a contact between a sphere and a plane. The two models briefly presented in the previous section validated in the research conducted for other papers, such as [16], were used in order to estimate the surface energy of the CrN thin films. The value of 18 nm was used in all computations for the AFM tip radius, R. The results obtained using the JKR model for the maximum value and the DMT model for the minimum value of the surface energy are summarized in table 4 and show a variation up to approximately three times of surface energy values.

Table 4. Surface energy γ of all CrN investigated samples.

γ [J/m^2]	Sample						
	CrN1	CrN2	CrN3	CrN4	CrN5	CrN6	CrN7
Minimum value	0.509	0.566	0.613	0.797	0.934	1.180	0.601
Maximum value	0.761	0.824	0.894	1.349	1.346	1.648	1.102

5. Conclusions

The elaboration using different deposition parameters determines preferential orientation of the atoms planes causing different material properties. The results concerning the impact of deposition parameters on the adhesion force for CrN thin films deposited by reactive magnetron sputtering on silicon substrate have shown that all varied parameters influence the adhesion force. The conducted tests allowed identifying the parameters which have greater influence than others.

The tests have shown that the adhesion force decreases with the increase of temperature. It also decreases when the pressure decreases and the temperature increases. However, the influence of the pressure is greater than the influence of the temperature, fact proven by the increase of the adhesion force seen when the pressure increases despite the temperature increase. The experimental investigations have also shown that the adhesion force decreases with the increase of nitrogen flow at constant ambient temperature. However, the influence of the pressure is greater than the influence of the nitrogen flow, fact proven by the increase of the adhesion force seen when the pressure increases despite the nitrogen flow increase.

The conducted tests using the XE 70 AFM and the interpretation of the obtained results using the XEI Image Processing Tool for SPM program allowed the characterization of the roughness of each sample and pointed out which mathematical models are suitable for the contact between the AFM tip and the sample surfaces. Using the chosen models the surface energy of the CrN thin films was determined and the results showed that it can vary up to three times depending on the deposition parameters of the sample.

6. References

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