บทความวิจัย

ผลของเวลาการเคลือบที่มีต่อโครงสร้างและสมบัติของฟิล์มบางโครเมียมไนโตรด์ที่ถูกสปัตเตอร์ด้วยวิธีรีแอคตีฟดีซีแมกนีตรอน

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บทคัดย่อ

ฟิล์มบางโครเมียมไนไตรด์ที่มีโครงสร้างระดับนาโนในงานวิจัยนี้จะเคลือบลงบนวัสดุรองรับที่เป็นแผ่นซิลิกอนด้วยวิธีรีแอคตีฟแมกนีตรอนสปัตเตอริงจากเป้าสารเคลือบโลหะโครเมียม ที่เวลาในการเคลือบแตกต่างกัน โดยแปรค่าเวลาการเคลือบจาก 60 นาที จนถึง 180 นาที ในงานวิจัยนี้จะศึกษาผลของเวลาในการเคลือบที่มีต่อโครงสร้างผลึก ลักษณะพื้นผิว ความหนา และ องค์ประกอบทางเคมี ฟิล์มบางที่เคลือบได้นำไปวิเคราะห์ลักษณะเฉพาะด้วยเทคนิค X-ray Diffraction (XRD), Atomic Force Microscopy (AFM) และ Energy Dispersive X-ray Spectroscopy (EDS) ผลการทดลองพบว่าโครงสร้างผลึก ลักษณะพื้นผิว ความหนา และองค์ประกอบทางเคมีสัมพันธ์กับเวลาในการเคลือบ โดยพบการเลี้ยวเบนรังสีเอกซ์ระนาบ (111) (200) และ (220) ของโครงสร้างโครเมียมไนไตรด์ เมื่อเวลาในการเคลือบมากขึ้นฟิล์มบางมีความเป็นผลึกมากขึ้นและมีขนาดผลึกเพิ่มขึ้น โดยขนาดผลึกมีค่าแปรตามเวลาในการเคลือบ ค่าคงที่แลตทิซสอดคล้องกับค่ามาตรฐาน JCPDS ทั้งนี้พบว่าเกรนมีขนาดใหญ่ขึ้น ค่า RMS roughness และ ความหนามีค่าเพิ่มขึ้นจาก 9 เป็น 42 nm และ 832 เป็น 2342 nm ตามลำดับเมื่อเพิ่มเวลาในการเคลือบ สุดท้ายปริมาณธาตุโครเมียมและไนโตรเจนมีค่าอยู่ระหว่าง 42.58 ถึง 46.26 at.% และ 53.74 ถึง 57.42 at.% ตามลำดับ

คำสำคัญ: เวลาการเคลือบ รีแอคตีฟ แมกนีตรอน สปัตเตอริง ฟิล์มบางโครเมียมไนไตรด์

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Effect of Deposition Time on Crystal Structure and Properties of Reactive DC Magnetron Sputtered CrN Thin Films

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ABSTRACT

Nanocrystalline CrN thin films have been deposited on unheated silicon substrates by reactive dc magnetron sputtering from a metallic Cr target, using different deposition time varied from 60 to 180 min. The effect of deposition time on the crystal structure, surface morphologies, thickness and chemical composition of the sputtered thin films has been established. Overall characterization of the samples has been performed by X-ray Diffraction (XRD), Atomic Force Microscopy (AFM) and Energy Dispersive X-ray Spectroscopy (EDS). Results from the experiments show that the crystal structure, surface morphology, thickness and chemical composition were found to depend directly on the deposition time. The polycrystalline CrN with (111), (200) and (220) planes were investigated. The longer deposition time enhances the crystallinity and crystal size of the films. The crystal size depended on the deposition time. The lattice constant was in good agreement with JCPDS standard. The grain aggregation with increasing of RMS roughness and thickness from 9 - 42 nm and 832 - 2342 nm, respectively, through the longer deposition time was observed. The Cr and N contents in the films were varied from 42.58 to 46.26 at.% and 53.74 to 57.42 at.%, respectively.

Keywords: Deposition time Reactive magnetron sputtering CrN thin films

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Introduction

Nowadays, there is a great deal of interest in using thin films of transition metal nitrides in many cutting and forming tools forging and die casting dies [1-3] application because of their high hardness, good wear resistance, low friction coefficient and chemical stability [4,5], lower thermal expansion, lower thermal conductivity and enhanced erosion resistance [6]. These films are extensively employed to increase the material surface properties and their corrosion resistance [7] resulting in the decrease of the tool costs and extended the tool life.

Chromium nitride (CrN) is a good candidate typically used protection film exhibiting good mechanical properties, high corrosion resistance, high oxidation resistance and low thermal conductivity [8-10]. Moreover some researchers show that the CrN has outstanding thermal stability [11-13]. Nowadays, it is applied on a large scale as an industrial coating on combustion engine components and metal forming tools. Therefore, besides being widely used in the mechanical manufacturing industry, chromium nitride coatings have a promising prospect for the applications in biology [14], photo-electronic device [15] and green-energy [16].

It is recognized that chromium nitride thin films may be formed such as Cr, Cr+Cr_2N, Cr_2N, Cr_2N+CrN and CrN, which different physical and mechanical properties could be obtained by appropriate selection of deposition conditions. CrN has face-centered cubic structure and theoretical density of 6.1 g/cm^3, while Cr_2N has a hexagonal structure and theoretical density of 6.5 g/cm^3 [17]. CrN thin films were fabricated using several deposition techniques, such as e-beam evaporation [18], arc ion plating [19], ion beam enhanced deposition [20] and magnetron sputtering, etc. However, Magnetron sputtering is a widely used physical vapor deposition (PVD) technique for CrN thin film depositions because of its low deposition temperature, high deposition rate and high control ability for the growth of the films [21]. These physical quantities are usually influenced by the chemical composition, phase content, and microstructure, which are dependent on the deposition conditions and preparation method such as bias voltage, pressures, plasma power, temperature, flow rates of gases and temperature.

Several researchers published data on reactive magnetron sputtered CrN thin film consider the effect of deposition parameters on their crystal structure, surface morphology and properties. However, only few studies correlated to the deposition time with the crystal structure and properties of the films. For this reason, the aim of this paper is to investigate how different variables of the deposition time can affect the crystal structure, crystal size, lattice constant, surface morphology, roughness value, thickness and element composition of CrN thin film. In particular, the relationships between the deposition time and the crystal structure and the properties were taken into account.

Materials and methods

Deposition of CrN thin films

Chromium nitride thin films were synthesized by home-made reactive DC magnetron sputtering in an unbalanced system as shown in Fig 1. The chamber was pumped by using a system of rotary and diffusion pumps. The flow of Ar and N_2 gases with 99.999% and 99.995% purity was controlled by separate mass flow controllers, respectively. A Chromium target with 99.97% purity was powered by the DC power suppliers. The silicon wafers (100) plane was used as substrate. Prior to deposition, the samples were first ultrasonically chemical cleaned in acetone and isopropanol solution for 15 min to remove the surface contaminants, then dried rapidly, and finally placed in the chamber. The target and the substrate were kept facing each other. The distance between the target and substrate was 150 mm. Before the deposition of the thin film, the air was evacuated from the deposition chamber reach to base pressure by rotary and diffusion pumps. The CrN thin films were deposited using corresponding sputtering conditions as listed in Table 1. The working pressure was kept constant at 4.0×10^{-3} mbar. The target power was kept at 345 W. The Ar and N_2 partial pressure flux was kept constant at 1.0×10^{-3} and 3.0×10^{-3} mbar, respectively by adjusting the Ar and N_2 flows during the deposition.

Characterization of CrN thin films

Crystal structural analysis was identified by X-ray Diffraction (XRD), Rigaku rint 2000. To investigate the crystal structure, crystal orientation and crystallite size of obtained films, a diffractometer was used in a Bragg-Brentano geometry ($\theta-2\theta$ geometry), at room temperature, with Cu Kα radiation (K = 1.5406 Å) with X-ray generator operated at 40 kV and 40 mA. A grazing angle of 2° with 2θ scan from 20^{O} - 80^{O} was applied for the phase identification. In order to investigate the dependence of deposition time on crystallite size of the CrN thin films, the crystallite size (D) within the films was calculated from Scherrer's formula as follow

$$D = (K\lambda)/(\beta\cos\theta)$$

Where D represents the crystallite size (nm), K is a dimensionless shape factor, and it is 0.94 for cubic crystal lattices, λ is the incident wavelength of the X-ray (for CuKα = 1.54056 Å), β is the full width at half maximum (FWHM) of the peak intensity in radian, and θ is the Bragg angle of the diffraction peak.

The surface morphology, surface roughness and thickness of CrN thin films were determined by Atomic force microscope (AFM) (Nanoscope IV, Veeco instruments Inc.) operating in the tapping mode. The chemical composition of the as-deposited films was determined by Energy Dispersive X-ray spectroscopy (EDS: EDAX) equipped on Scanning Electron Microscopy (SEM: LEO 1450VP).

Table 1 The deposition conditions of CrN thin films.

Parameters	Value
Target	Cr (99.97%)
Sputter gas	Argon (99.999%)
Reactive gas	Nitrogen (99.995%)
Base Pressure (mbar)	5.0×10^{-5}
Working Pressure (mbar)	4.0×10^{-3}
Cathode current (mA)	800
Cathode power (W)	345
Ar partial pressure (mbar)	1.0×10^{-3}
N_2 partial pressure (mbar)	3.0×10^{-3}
Distance from cathode to substrate (mm)	150
Substrate	Silicon (100)
Deposition time (min)	60, 120, 180

Figure 1 Home-made DC magnetron sputtering.

Results

1. Effect of deposition time on Crystal Structure

Fig. 2 shows the XRD patterns for the CrN thin films deposited at deposition time ranging from 60 to 180 min. The XRD patterns of samples showed that the crystal structure of CrN samples was dramatically affected by the variation of the deposition time. For the film grown with the lowest deposition time values of 60 min, the peaks are located at values of 2θ equal to 37.52°, 43.14° and 63.10°, respectively. All peaks can be ascribed to the diffraction from the (111), (200) and (220) planes of the face-centered cubic (fcc) binary nitride chromium nitride phase (JCPDS file no. 77-0047). The preferred orientation of (111) was found for this condition. The intensity for the (111) and (200) planes was constant whereas the increase of intensity at (220) plane for the CrN thin film deposited at longer deposition time of 120 min was obtained. The continuous increase of intensity at (220) plane was investigated at the longest deposition time of 180 min.

Another important consequence of the deposition times is the change in the crystal structure features especially, the crystallite size of the films. The crystallite size determined using the Scherrer formula increased gradually with increasing deposition time (Table 2). For instance, the crystallite size increased from 27 nm to 32 nm for 60 and 180 min of deposition time, respectively. The lattice constants obtained from X-ray diffraction pattern of the films was in the range of 4.155 - 4.160 Å through the deposition time in good agreement with the JCPDS standard.

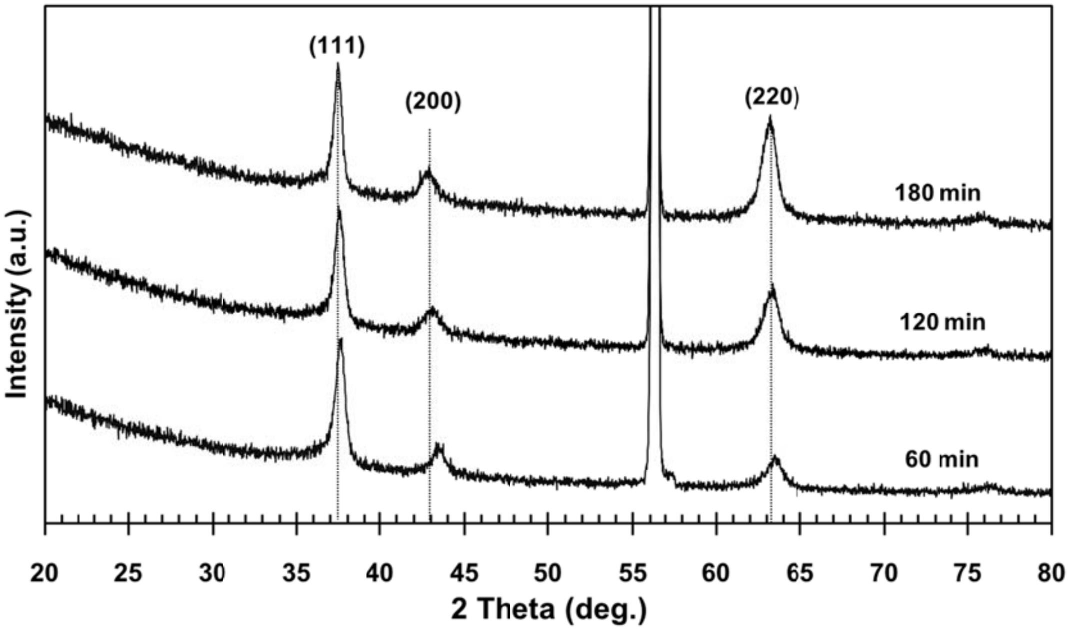


Figure 2 XRD patterns of CrN thin films deposited at different deposition times.

Table 2 Deposition parameters and results of CrN thin films deposited at different deposition times.

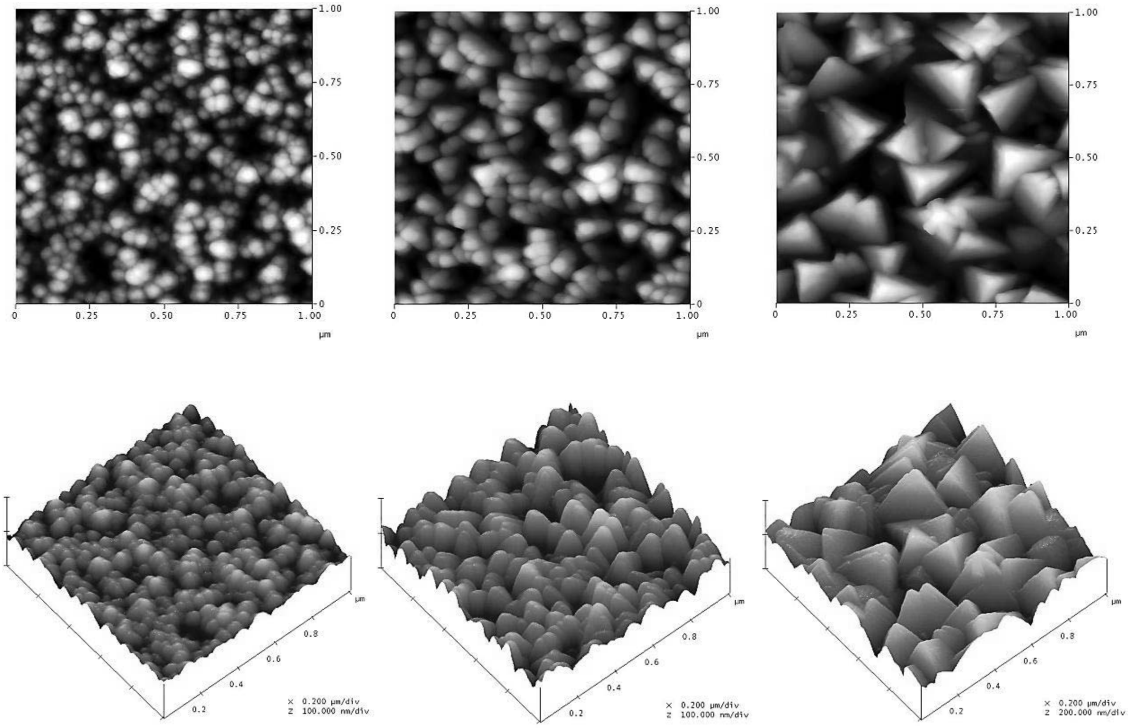
Deposition time (min)	Crystal size (nm)	Lattice constant (Å)	Composition (at.%)			Thickness (nm)	RMS roughness (nm)
			Cr	N	Cr:N		
60	27	4.158	42.58	57.42	0.74	832	9
120	30	4.155	44.87	55.13	0.81	1575	20
180	32	4.160	46.26	53.74	0.86	2342	42

2. Effect of deposition time on surface morphology, surface roughness and thickness

The two and three-dimensional AFM images of CrN thin films deposited at different deposition times according to the results in Table 2 were presented in Fig 3. Surface morphology and surface roughness (RMS) as a function of the deposition time, the increase of deposition time also affected the grain structure and morphology obtained from the AFM data as shown in Fig. 3. A small with spherical shape of grains were found in the films deposited at the lowest deposition time of 60 min. Moreover, the same size of individual grain which spread across the surface was also obtained (Fig 3a). As the increase of the deposition time to 120 min, the grains evolutions were investigated. The grains morphologies were changed to the needle-like shape. The various grain sizes were distributed on the surface. The grains with a bigger size in comparision with the films deposited at 60 min were also found (Fig 3b). When the deposition time increased to 180 min, the grain morphologies became a pyramid shape. The grain sizes were the biggest with random orientation on the surface (Fig 3c).

In order to study the surface features of CrN thin films, it is necessary to measure the main surface roughness parameters of the films, namely the root mean square (RMS). These RMS values are correlated with the grains distribution. The RMS roughness of the films deposited at deposition time of 60, 120 and 180 min were in the range of 9 to 42 nm as clearly seen in the Table 2 and Fig. 5. The lowest roughness was achieved at deposition time of 30 min. The roughness value was increased reach to 20 nm when deposition time was increased to 120 min. The same trend roughness value enhancement with the highest value of 42 nm was investigated for the longest deposition time of 180 min. It is clear that CrN films prepared at shorter deposition time have a smooth surface while CrN thin films formed at longer deposition time exhibit more roughness.

Fig. 4 represents the variation of films' thickness vs. deposition time obtained from 2D section analysis of AFM image. It can be seen that using the different deposition time, the thickness value of CrN thin films shows an obvious rise with increasing deposition time. At low deposition time of 60 min, the thickness was 832 nm. When the deposition time is longer (120 min), the thickness value of films were increased to 1575 nm. The thickest film value of 2342 nm was investigated for the film deposited at the longest deposition time of 180 min.



a
60 min

b
120 min

c
180 min

Figure 3 Surface morphology of CrN thin film deposited at different deposition times.

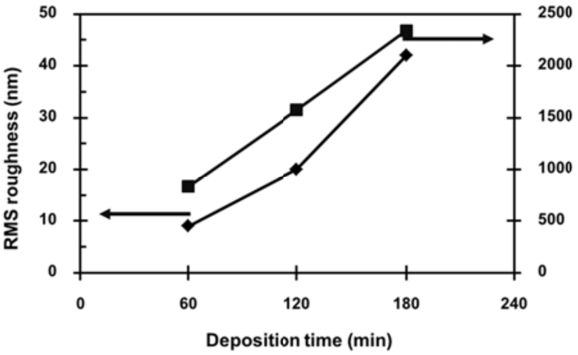


Figure 4 RMS roughness and thickness of CrN thin films deposited at different deposition times.

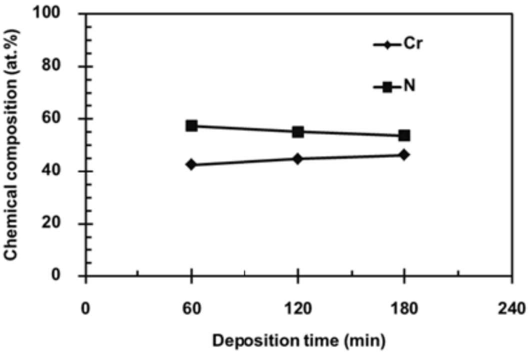


Figure 5 Chemical composition of CrN thin films deposited at different deposition times.

3. Effect of deposition time on element composition

The chemical composition of the CrN thin films analyzed from EDS technique was presented in Fig 5. The EDS results indicated that the deposition time plays a role in the chemical composition of chromium and nitrogen. The Cr contents were increased whereas the N contents were decreased by increasing the deposition time from 60 – 180 min. The Cr content increases from 42.58 to 46.26 at.% but N content decreases from 57.42 to 53.74 at.% through longer deposition time. In addition, stoichiometric of CrN thin fims deposited at different deposition time was represented in Table 2. The stoichiometric CrN compound is characterized by a ratio of Cr/N content. The stoichiometry was in the range of 0.74 - 0.86.

Discussion and Conclusion

The nanostructure CrN thin films were successfully fabricated on glass slide and single crystal silicon (100) substrates by using the direct current reactive magnetron sputtering. XRD results showed that face-centered cubic CrN phase can be observed in films with the different deposition time. The crystallinity of the films was improved with the deposition time. The preferred orientation of (111) plane was observed for all conditions. The crystal size obtained from Scherrer's formula was increased from 27 to 32 nm through the deposition time. The lattice constant of the film was varied from 4.155 – 4.160 Å with good agreement of JCPDS standard of the CrN structure (JCPDS file no. 77-0047). AFM observations showed that the surface morphology and surface roughness are proportional to the deposition time. The bigger grain size and rougher surface were obtained by increasing the deposition time from 60 – 180 min with RMS roughness value enhanced from 9 – 42 nm, respectively. The effect of deposition time on the deposition rate showed that the film thickness was increases from 832 -2342 nm. The Cr and N contents in the films varied from 42.58 to 46.26 at.% and 53.74 to 57.42 at.% were obtained from EDS results.

The XRD results indicated that the as-deposited thin films are face-centered cubic-CrN structure. The diffraction patterns were in good agreement with the standard JCPDS no. 77-0047. The crystallite sizes of the sample increased with the increasing the deposition time. The increase of the crystal size could be attributed to an increase in the cluster formation, which leads to agglomeration and grains coalesce together resulting in the larger grains formation with higher crystallinity [22]. Another reason is that the more thickness of the films, the more deposited materials diffract an incident X-ray beam and increase in the diffracted intensity [23]. Moreover, the lattice constant corresponded to the JCPDS data was also confirmed the as-deposited crystal structure as well.

The evolutions of small rounded grain to the large pyramid grain were found when increasing the deposition time. It was attributed to the larger number of deposited atom/molecule arriving at the substrate as increased deposition time resulting increased the adatom mobility and formation of nucleated cluster during deposition [9]. As increase deposition time, the RMS roughness value was enhanced due to agglomerate of particles and the consequently forming of new islands [24]. As a result, thin films also become rougher with increasing the deposition time, which is in good agreement with XRD data. Therefore, this can be explained by increasing the crystallinity and the crystallite sizes with increasing the deposition time. The 2D section analysis of AFM images show that the thickness of the films increasd with the increase in the deposition time. It was suggested that more deposited atoms are deposited on the substrate surface which can result in a thicker film [25]. This results indicated that the deposition time plays a role in the Cr and N contents. The Cr and N contents were changed as a function of deposition time.

References

1. Su, G., and Liu, Z. 2012. Wear Characteristics of Nano TiAlN-Coated Carbide Tools in Ultra-High Speed Machining of AerMet100. *Wear*. 289: 124-131.
2. Gnoth, C., Kunze, C., Hans, M., Baben, M., Emmerlich, J., Schneider, J. M., and Grund-meier, G. 2013. Surface Chemistry of TiAlN and TiAlNO Coatings Deposited by Means of High Power Pulsed Magnetron Sputtering. *Journal of Physics D: Applied Physics*. 46: 084003.
3. Chakrabarti, K., Jeong, J. J., Hwang, S. K., Yoo, Y. C., and Lee, C. M. 2002. Effects of Nitrogen Flow Rates on the Growth Morphology of Tialn Films Prepared by an RF Reactive Sputtering Technique. *Thin Solid Films*. 406: 159-163.
4. Barshilia, H. C., Deepthi, B., and Rajam K. S. 2006. Deposition and Characterization of Tialn/Si_3N_4 Superhard Nanocomposite Coatings Prepared by Reactive Direct Current Unbalanced Magnetron Sputtering. *Vacuum.* 81: 479-488.
5. Chan, Y. C., Chen, H. W., Chao, P. S., Duh, J. G., and Lee, J. W. 2013. Microstructure Control inTiAlN/SiN_x Multilayers with Appropriate Thickness Ratios for Improvement of Hardness and Anti-Corrosion Characteristics, *Vacuum* 87: 195-199.
6. Chen, J. T., Wang J., Zhang F., Fan X. Y., Wu Z. G., and Yan, P. X. 2009. Characterization and Temperature Controlling Property of Tialn Coatings Deposited by Reactive Magnetron Co-Sputtering. *Journal of Alloys and Compounds*. 472: 91–96.
7. Devia, D. M., Restrepo-Parra, E., Arango, P. J., Tschiptschin, A. P., and Velez, J. M. 2011. TiAlN Coatings Deposited by Triode Magnetron Sputtering Varying the Bias Voltage. *Applied Surface Science*. 257: 6181-6185.
8. Polcar, T., Parreira, N. M. G., and Novák, R. 2007. Friction and Wear Behaviour of CrN Coating at Temperatures up to 500 °C. *Surface and Coatings Technology*. 201: 5228-5235.
9. Pradhan S. K., Nouveau, C., Vasin, A., and Djouadi, M. -A. 2005. Deposition of CrN Coatings by PVD Methods for Mechanical Application. *Surface and Coatings Technology*. 200: 141-145.
10. Xu, J., Umehara, H., and Kojima, I. 2002. Effect of Deposition Parameters on Composition, Structures, Density and Topography of CrN Films Deposited by R.F. Magnetron Sputtering. *Applied Surface Science*. 201: 208-218.
11. Chen, H. -Y., and Lu, F. -H. 2006. Oxidation Behavior of Chromium Nitride Films. *Thin Solid Films*. 515: 2179-2184.
12. Lee, D. B., Jang, Y. D., Myung, H. S., and Han, J. G. 2006. High-Temperature Oxidation of Magnetron-Sputtered Cr–N-Coated Steels. *Thin Solid Films*. 506: 369-372.

13. Mayrhofer, P. H., Tischler, G., and Mitterer, C. 2001. Microstructure and Mechanical/Thermal Properties of Cr–N Coatings Deposited y Reactive Unbalanced Magnetron Sputtering. *Surface and Coatings Technology*. 142: 78-84.
14. Major, B., Bruckert, F., Lackner, J., Ebner, R., and Kustosz R. 2008. Coatings on TiN and Ti (C, N) Basis for Biomedical Application to Blood Contact and Tin/CrN Multilayered Tribological Systems Produced by Pulsed Laser Deposition. *Archives of Metallurgy and Materials*. 53: 39-48.
15. Lee, S., Ha, J., Lee, H., Lee, H., H. Goto, Hanada, T., Goto, T., Fujii, K., Cho, M., and Yao, T. 2009. Leakage Current Improvement of Nitride-Based Light Emitting Diodes Using CrN Buffer Layer and Its Vertical Type Application by Chemical Lift-Off Process. *Applied Physics Letters*. 94: 082105.
16. Nam, N., and Kim, J. 2007. Electrochemical Behavior of CrN Coated on 316L Stainless Steel in Simulated Cathodic Environment of Proton Exchange Membrane Fuel Cell. *Japanese Journal of Applied Physics*. 47(8): 6887-6890
17. ASM Engineering Materials Reference Book, ASM International, 1989.
18. Avelar-Batista, J. C. Spain, E., Housden, J., Fuentes, G. G., Rodriguez, R., Montala´, F., Carreras, L. J., and Tate, T. J. 2005. Effect of Coating Thickness and Deposition Methods on The Stripping Rate of Cr–N Coatings. *Surface & Coatings Technology*. 200: 1842-1848.
19. Huang M. D., Liu, Y. Meng, F.Y. Tong, L. N., and Li, P. 2013. Thick CrN/TiN Multilayers Deposited by Arc Ion Plating. *Vacuum*. 89:101-104.
20. Yongqing, F., Xiaodong, Z., Bin, T., Xinfang, H., Jiawen, H., Kewei, X., and Batchelor, A.W. 1998. Development and Characterization of CrN Films by Ion Beam Enhanced Deposition for Improved Wear Resistance *Wear*. 217: 159-166.
21. Lin, J, Sproul, W. D., Moore, J. J., Lee, S. and Myers, S. 2011. High Rate Deposition of Thick CrN and Cr_2N Coatings Using Modulated Pulse Power (MPP) Magnetron Sputtering. *Surface and Coatings Technology*. 205: 3226-3234.
22. Ghorannevis, Z. Akbarnejad, E., and Ghoranneviss, M. 2016. Effects of Various Deposition Times and RF Powers on Cdte Thin Film Growth Using Magnetron Sputtering. *Journal of Theoretical and Applied Physics*. 10(3): 225-231.
23. Chekour, L., Nouveau, C., Chala, A., Labidi, C., Rouag, N, and Djouadi, M. A. 2005. Growth Mechanism for Chromium Nitride Films Deposited by Magnetron and Triode Sputtering Methods. *Surface and Coatings Technology*. 200: 241-244.

24. Ahmadpourian, A. Luna, C., Boochani, A., Arman, A., Achour, A., Rezaee, S., and Naderi, S. 2016. The Effects of Deposition Time on Surface Morphology, Structural, Electrical and Optical Properties of Sputtered Ag-Cu Thin Films. *The European Physical Journal Plus*. 131: 381-387.
25. Patel, K. H., and Rawal S. K. 2017. Synthesis and Characterization of Sputtered Nanostructured ZnO Films: Effect of Deposition Time and Pressure on Contact Angle Behavior of Ethylene Glycol and Water. *Advance Materials Letters.* 8(2): 101-106.

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