Effect of Power and Nitrogen Content on the Deposition of CrN Films by Using Pulsed DC Magnetron Sputtering Plasma*

Umm-i-KALSOOM1, R. AHMAD1, Nisar ALI1, I. A. KHAN2, Sehrish SALEEM1, Uzma IKHLAQ1, Nasarullah KHAN1

1Department of Physics, Govt. College University, Lahore 54000, Pakistan
2Department of Physics, Govt. College University, Faisalabad 38000, Pakistan

Abstract CrN thin films are deposited on stainless steel (AISI-304) substrate using pulsed DC magnetron sputtering in a mixture of nitrogen and argon plasma. Two set of samples are prepared. The first set of sample is treated at different powers (100 W to 200 W) in a mixture of argon (95%) and nitrogen (5%). The second set of samples is treated at different nitrogen concentrations (5% to 20%) in argon (95% to 80%) for a constant power (150 W). X-ray diffraction (XRD) analysis exhibits the development of new phases related to different compounds. The crystallinity of CrN varies by varying the applied power and nitrogen content. Crystallite size and residual stresses of the CrN (111) plane show similar variation for the applied power and nitrogen contents. Scanning electron microscopy (SEM) analysis shows the formation of a granular surface morphology that varies with the change of powers and nitrogen content. The thickness of the film is measured using SEM cross sectional images and using atomic force microscopy (AFM) scratch analysis. The maximum film thickness (about 755 nm) is obtained for the film deposited at 5% nitrogen in 95% argon at 150 W power. For these conditions, maximum hardness is also observed.

Keywords: sputtering, crystallinity, morphology, thickness, roughness

PACS: 52.77.Dq, 52.50.Dg, 81.15.-z, 52.50.-b

DOI: 10.1088/1009-0630/15/7/12

1 Introduction

Thin films of chromium nitride (CrN) have been reported for many years due to its outstanding industrial applications. CrN is an attractive material to wear and corrosion protection for bright and non-tarnishing surfaces due to good wear resistance, low friction coefficient and high hardness, corrosion resistance and thermal barrier properties [1,2].

Researchers around the world are depositing CrN films on different substrates using diverse deposition techniques such as electro-deposition, physical vapor deposition (PVD), sputtering, and magnetron discharges. The electro-deposition technique is used to produce carcinogenic hexavalent Cr+6 from CrO3 while other above mentioned techniques are being used to avoid such types of carcinogenic elements since sputter deposition involves the transfer of atoms only, instead of ions [3]. PVD and magnetron discharge techniques produce high quality films since high energy ions are used to deposit thin films on different substrates and the quality of the films may change by changing the operating parameters of the device [4,5].

In the present work, CrN thin films are deposited by using a pulsating DC magnetron sputtering technique by varying the argon to nitrogen ratio and applied power. Phase identification, crystallinity, crystallite sizes, residual stresses, surface morphology, film surface roughness, and hardness of the deposited CrN films are characterized by using X-ray diffraction (XRD), a scanning electron microscope (SEM), an atomic force microscope (AFM) and Vicker’s hardness techniques, respectively. Additionally, the roles of diverse concentration of argon and nitrogen gases in the vacuum chamber and different applied powers on the film surface properties are also investigated.

2 Experimental setup

CrN thin films are deposited on stainless steel (AISI-304) substrates in argon and nitrogen (99.96% pure) plasma using a pulsating DC magnetron sputtering technique with pulses of frequency 100 Hz. Fig. 1 exhibits the systematic arrangement of the pulsating DC magnetron sputtering system. The target and substrate are placed in a stainless steel vacuum chamber, which is evacuated to a base pressure of 10−3 mbar and, during deposition, the gas pressure is kept at 1 mbar. The electrode system consists of two parallel plate electrodes, one electrode (made of chromium with 99.98% purity) acts as the target with magnets arranged behind it (Fig. 2) and also serves as the cathode, and the other electrode (made of stainless steel) acts as holder for the substrate (AISI-304) and as the anode. Both electrodes are circular in shape having dimensions 9×2 cm². The substrate-to-target distance is

*supported by the Higher Education Commission (HEC) of Pakistan
3 cm, which remains constant throughout the experiment. Two set of samples are treated: (i) samples have been treated with 100 W, 150 W, and 200 W powers at constant argon (95%) to nitrogen (5%) ratio; and (ii) samples have been treated for different argon (95%, 90%, 85%, 80%) to nitrogen (5%, 10%, 15%, 20%) ratio at constant power (150 W). Prior to the deposition, the samples are polished with abrasive SiC paper with fine (from 300 to 2000) grits. After that, these samples are rinsed ultrasonically in acetone for 30 min.

3 Results and discussions

3.1 XRD analysis

Figs. 3 and 4 exhibit the XRD patterns of untreated and treated samples. XRD patterns of the untreated sample show the presence of an face centered cubic (fcc) austenitic stainless steel (γ-Fe) phase and a body centered cubic (bcc) ferritic iron (α-Fe) phase. The diffraction peaks having (111), (200) and (220) plane reflections are related to the γ-Fe phase whereas diffraction peaks having (110) and (200) plane reflections are related to the α-Fe phase. A rise in temperature during polishing may cause stress induced transformation of γ to α phase [6,7].

![Fig.3 XRD patterns of untreated and CrN deposited AISI-304 at different powers (100 W, 150 W, 200 W) for constant argon (95%) to nitrogen (5%) ratio](image)

![Fig.4 XRD patterns of untreated and CrN deposited AISI-304 for different nitrogen concentrations (5%, 10%, 15%, 20%) in argon (95%, 90%, 85%, 80%) at constant power (150 W)](image)
substrate surface. A broad peak indicates the formation of nano-crystallites since peak broadening is inversely related to crystallite size. For 150 W applied power, the α phase disappears and new phases of Cr$_2$N (221) and Fe$_3$N (112) planes are formed. For the same power, the increase in peak intensity of CrN (111) plane is also observed. It is interesting to note that peak intensity related to CrN (111) plane increases while the peak intensities of the γ and α phases decrease. From the XRD patterns obtained for 200 W applied power we have made the following observations: (i) increases in the crystallinity of CrN (220) plane; (ii) appearance of Fe$_3$N (101) plane showing better crystallinity; and (iii) re-improvement in the crystallinity of (γ, α) phases.

It is clear that the maximum peak intensity of CrN (111), γ and α phases is observed for 200 W applied power. The increase in peak intensity of α and γ phases is due to the incorporation of energetic nitrogen ions. The energy of the impinging ions increases by increasing applied power, which enhances the incorporation of nitrogen and reaction between the species leads to the growth of nitrides of chromium. As a result, we have the preferential sputtering of target material [8-11]. The decrease in peak intensity of the γ-phase at 150 W power is due to the increase in peak broadening caused by defects and micro-strains developed during the deposition process [12,13].

Fig. 4 exhibits the second set of samples treated for different concentrations of argon to nitrogen ratio for fixed applied power (150 W) and pressure (1 mbar). For 5% nitrogen in 95% argon, the peak related to the α phase at an angle of 64.44° disappears. Peak intensities related to γ-phase decrease and new peaks related to CrN (111) and Cr$_2$N (221) appear. The disappearance of the α phase and the decrease in peak intensity of the γ-phase is associated with the formation of sufficiently thick film on the substrate surface [14]. However, a rise in surface temperature due to energy deliverance during the deposition process is associated with the formation of new phases of chromium nitride [15]. These newly formed nitrides are of nano-dimensions since peaks are more broadened. For 10% nitrogen, peak intensities of all the phases observed for 5% nitrogen increase along with the formation of CrN (220) and Fe$_3$N (110) phases. For 15% nitrogen, peak intensities of newly formed nitrides increase along with the appearance of Fe$_3$N (101) and (112) planes. For 20% nitrogen, the intensities of all peaks related to different phases are decreased. It is clear that the crystallinity and nucleation of different compounds vary by changing the nitrogen contents in the deposited films.

Fig. 5 (a) and (b) demonstrates the crystallite size of the CrN (111) plane as a function of both power and concentration. Debye Scherrer formula [12] is employed to estimate the crystallite size of the CrN (111) plane as a function of both power and concentration.

\[
\text{Crystallite size} = \frac{K\lambda}{(FWHM)\cos\theta},
\]

where \(K\) is a numerical constant \((K = 0.93)\), \(\lambda\) is the wavelength of incident radiation \((\lambda = 1.5406 \text{ Å})\), \(FWHM\) is the full width at half maxima, and \(\theta\) (rad) is the Bragg's angle.
while for higher nitrogen contents, its crystallite size starts to decrease. This shows that more nitrogen content enhances the diffusion level into the substrate as well as creating more defects, lattice distortion, and formation of nano-crystallites that leads to peak broadening [12].

XRD data are also employed to estimate the residual stresses developed in the films during deposition process, which are indicated by the shift of diffraction peaks from their stress-free data. During the deposition process, enough energy is delivered to the substrate by the impinging ions, which raises the substrate surface temperature and in turn causes lattice distortion and changes d-spacing due to the differences in inter-atomic distances and thermal and expansion coefficients [19,20]. The peak shifting to the lower angular position is due to the small grain size indicated by peak broadening, which gives rise to compressive residual stresses. The shifting to a higher angle indicates tensile stresses [21,22].

The in-plane residual coating stress $\sigma$ causes a widening of the lattice and therefore a displacement $(d - d_0)$ of the respective XRD peak.

$$\varepsilon = \frac{(d - d_0)}{d_0}, \quad (2)$$  

where $d$ is the observed value and $d_0$ is the standard plane spacing in our case of the CrN (111) and $\varepsilon$ is the strain induced in the coating.

The Young’s modulus ($E$) of CrN is 400 GPa, residual stress produced in the film can be calculated using the simple relation

$$\sigma = \varepsilon E. \quad (3)$$

Fig. 6(a) and (b) show the variations of residual stresses developed in the CrN (111) plane with both applied powers and nitrogen concentrations. Fig. 6(a) shows the effect of nitrogen concentrations on the residual stresses developed in CrN films during deposition process. For 5% nitrogen content, compressive stresses (~0.99 GPa) are obtained in the CrN (111) plane, which are transformed to tensile stresses (0.69 GPa) for 10% nitrogen content [23]. After that, these tensile residual stresses are again transformed to compressive [13] sharply for 15% nitrogen and slowly for 20% nitrogen contents.

Fig. 6(b) shows that compressive residual stresses developed in CrN films deposited for 100 W, 150 W and 200 W applied powers change from ~4.78 GPa to ~5.45 GPa and ~2.98 GPa, respectively. It is worth noting that the maximum compressive residual stresses observed for 150 W powers are due to smaller crystallite sizes [24,25] (Fig. 5), since smaller crystallite size provides more boundary area, which slows down the slip motion and thus results in higher residual stresses and strength of the material. The increase of power increases the adatom mobility, which promotes atomic migration to grain boundaries causing crystal growth, which in turn induces the relaxation in compressive stresses [15].

Such variation in residual stresses for different applied powers and nitrogen concentrations is associated with variation in crystallites, defects, peak intensity, and rise in surface temperature during energetic nitrogen ion bombardment. These parameters are associated with applied powers and nitrogen concentrations. These results agree well with the observations on XRD patterns.

### 3.2 SEM analysis

Fig. 7 shows the SEM microstructural features of the samples treated for different applied powers (100 W, 150 W, and 200 W). The micrograph of the CrN film deposited for 100 W power demonstrates the formation of rounded grains of uniform distribution. There are some irregular but long tracks of empty space resulting in the decrease of film porosity. The micrograph of CrN film deposited for 150 W power displays again the formation of rounded grains, which are distributed uniformly on the substrate. However, the film is more compact since the area covered by the empty tracks is comparatively smaller. The micrograph of CrN film deposited for 200 W powers exhibits the formation of long fiber-like patterns whose dimensions are
It is clear that film porosity and distribution of grains vary with increasing applied powers and the results agree well with the XRD results. The surface morphology is directly associated with the deposition parameters and film growth, in turn, depends on the energy deliverance to the substrate surface and consequently the rise in surface temperature due to ion bombardment. Moreover, the empty tracks observed in the film are due to the vacancies which enhance the diffusion process \cite{26}. More diffusion applies more residual stresses to the film. The long empty tracks forming vertical columns are due to the presence of residual stresses \cite{27,28}.

Cross-sectional SEM images are used for the measurements of film thickness. The following results are deduced: (a) at 100 W power, an average thickness of about 520 nm is observed (Fig. 9); (b) average thickness value is increased to 760 nm with the increase of power up to 150 W; and (c) with the further increase of power to 200 W decrease in average thickness (250 nm) is observed.

Cross-sectional SEM images are used for the measurements of film thickness. The following results are deduced: (a) at 100 W power, an average thickness of about 520 nm is observed (Fig. 9); (b) average thickness value is increased to 760 nm with the increase of power up to 150 W; and (c) with the further increase of power to 200 W decrease in average thickness (250 nm) is observed.

**3.3 AFM analysis**

AFM is employed to investigate the effects of applied powers and nitrogen concentration on the film thickness and roughness.

Fig. 10(a) and (b) show the film thickness and roughness both as a function of applied power (100 W to 200 W) for constant nitrogen (5%) concentration and as a function of different nitrogen concentrations (5% to 20%) in argon for constant power (150 W), respectively.
The main features are: (a) both thickness and roughness first increase up to 150 W power and then decrease for higher power (200 W); (b) maximum film thickness and roughness are obtained for 150 W power; and (c) minimum film thickness and roughness are obtained for 200 W power. Similar variation in the thickness is observed from the cross-sectional SEM imaging, having approximately the same thickness values as observed from AFM measurements. Actually, the input power is related to the discharge current, which depends on the number of accelerated ions hitting the target material. At 100 W, the number of energetic chromium atoms sputtered from the target material is lower, resulting in the formation of thin film with low surface roughness [19]. At 150 W, energetic chromium atoms sputtered from the target material are more in numbers comparatively, thereby increasing the crystallinity and film thickness and in turn increasing the surface roughness. At 200 W, the atoms sputtered during higher input powers have sufficient energy and therefore would re-sputter the already developed film on substrate. This may result in the decrease of film thickness and roughness. In the case of increasing nitrogen concentration in argon, the minimum film thickness and roughness is observed at 10% nitrogen content and 150 W power. The reason for the decrease in thickness and roughness is the formation of a nitrided compound layer on the target surface (Cr) which reduces the metal sputtering yield or it may be due to the re-sputtering of the deposited film [30]. Roughly, thickness and roughness of the film are increased with the increase of the nitrogen concentration up to 20%, which may be due to more diffusion and deposition during high energy nitrogen ions bombardment on the chromium target surface [31,32]. Thus, one can conclude that the film thickness and roughness show a similar trend with increasing powers as well as with increasing nitrogen concentrations.

### 3.4 Hardness testing

Fig. 11(a) and (b) show the variation in the hardness of samples treated for different applied powers at constant nitrogen concentration (5%), and the variation in hardness for different nitrogen concentrations in argon at constant power (150 W). It is clear from the figure that the hardness value of treated samples is higher than that of the untreated samples. The micro hardness for untreated samples is found to be 309 HV. The variation in hardness is observed as follows. (a) Maximum surface hardness of 1182 HV is observed for 150 W, (b) the hardness value is decreased to 993 HV for 200 W. The hardness of film increases by the formation of dense and compact thick film with high compressive residual stresses along with small crystallite size [18,19,33], and we have observed a compact and crack-free film at 150 W power. The possible explanation for the decrease in micro hardness at 200 W power is due to the formation of thin film with less compressive residual stresses [21]. From Fig. 10(b) it is observed that (a) maximum hardness of 1182 HV is achieved at 5% N<sub>2</sub> in 95%Ar, (b) hardness value is reduced to 1026 HV by increasing nitrogen content to 10%, (iii) increase in hardness value (1125 HV) is observed with the increase of concentration up to 15%, (c) surface hardness decreases to 1050 HV with the increase of nitrogen to 20%. At 10% nitrogen the resultant film has compressive residual stresses but coarse surface morphology with minimum film thickness and low hardness. With the increase in surface hardness for 15% nitrogen concentration, the deposited film is more compact and fine grained, which can be observed from the SEM results. The decrease of hardness with further increase of N<sub>2</sub> percentage in argon plasma results from the presence of tensile residual stresses [20].

![Fig.10](image1.png)  
**Fig.10** Effect of input powers (100 W, 150 W, 200 W) for constant argon (95%) to nitrogen (5%) ratio, and effect of different nitrogen concentrations (5%, 10%, 15%, 20%) in argon (95%, 90%, 85%, 80%) on films thickness and roughness

![Fig.11](image2.png)  
**Fig.11** Variation of hardness with power (100 W, 150 W, 200 W) for constant argon (95%) to nitrogen (5%) concentration and variation of hardness for different N<sub>2</sub> concentrations (5%, 10%, 15%, 20%) in argon (95%, 90%, 85%, 80%) at constant power (150 W)
4 Conclusion

CrN films are successfully deposited on stainless steel (AISI-304) substrate using pulsed DC magnetron sputtering. X-ray diffraction patterns exhibit the development of new phases related to different compounds of chromium nitride. On the other hand, large CrN content is present in the film deposited for 10% nitrogen content at constant 150 W. Crystallite size of the CrN (111) plane and residual stresses depend on the variation of applied power and nitrogen contents. These parameters show similar trends with both applied powers and nitrogen contents. Scanning electron microscopy analysis shows the formation of granular surface morphology that varies with the changes of powers and nitrogen contents. SEM cross-sectional images and atomic force microscopic scratch analysis are used to measure the thickness of the deposited film. Thickness values measured through AFM and SEM give approximately the same results. Atomic force microscopic analysis reveals that variation in film thickness and roughness is directly related with process parameters. Vicker’s hardness testing shows the variation in hardness with change in the power and concentration of nitrogen in argon. The maximum film thickness (755 nm) and hardness (1182 HV) is obtained for films deposited at 150 W and 5% nitrogen contents.

Acknowledgements

We are thankful to Dr. I. M. GHAURI Director CASP, GC University, Lahore, for facilitating SEM analysis, and Dr. A. S. BHATTI, Dean of Sciences CIIT, Islamabad for AFM analysis.

References

(Manuscript received 21 October 2011)
(Manuscript accepted 13 March 2012)
E-mail address of corresponding author R. AHMAD: ahriaz@gcu.edu.pk