

Microstructural characterizations and hardness evaluation of d.c. reactive magnetron sputtered CrN thin films on stainless steel substrate

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Abstract. Chromium nitride (CrN) thin films were deposited on stainless steel (grade: SA304) substrate by using d.c. reactive magnetron sputtering and the influence of process parameters such as substrate temperature, pressure, and power on their microstructural characteristics were investigated in the present work. The CrN films were characterized with X-ray diffraction (XRD) to reveal the formation of different phases and its texture. The films showed the (111) preferred orientation but its intensity decreased, while intensity of peak (200) increased with increase in working pressure. The mixture of CrN and Cr₂N phases were identified at low working pressure and temperature. The preferred orientations of CrN thin films are strongly influenced by sputtering conditions, thickness, and the induced residual stress in the films as observed in the present work. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to characterize the morphology and surface topography of thin films, respectively. The study shows that the hardness of films strongly depends on the grain size and the film density, which are influenced by combined effect of the working pressure, temperature, and power of the sputtering process.

Keywords. CrN thin films; magnetron sputtering; microstructural characterization; microhardness.

1. Introduction

Transition metal nitrides based coatings such as TiN and CrN are extensively used in coating industries due to its excellent strength, wear, and erosion resistance. CrN has been identified as a better substitute for TiN coatings for tribological applications due to its superior wear resistance and corrosion resistance as reported in the literature (Safi 2000). Among the various techniques available for the deposition of CrN thin films, reactive magnetron sputtering could be used effectively to tailor the microstructural features of the films as a function of sputtering variables such as substrate temperature, gas pressure, and power. Chromium nitride coating (CrN), deposited by reactive magnetron sputtering, exhibits good mechanical properties such as high microhardness and low thermal conductivity, good wear and corrosion resistance. The microhardness of CrN films was found to be insensitive to variation in the deposition parameters due to shallower transitions in different phases (Hones *et al* 1997). Fabis *et al* (1990) investigated the CrN coating and using statistical technique ANOVA, they reported that the sputter-

ing pressure, substrate bias, and target power are vital parameters for tailoring the microstructure of the films with the desired properties. The mechanical and tribological properties of CrN coatings deposited under different ratios of sputtering gas and reactive gases are reported in the literature (Meunier *et al* 1998; Essen *et al* 2006; Fornies *et al* 2006). It has been reported that at low N₂ ($\leq 2\%$) concentration, pure Cr was detected in thin films while in N₂ concentration up to 40%, [Cr + N] – [Cr + CrN_x] – [Cr + CrN] phase sequence was found. Paternoster *et al* (2008) found that the annealing of CrN thin films in vacuum has induced phase transformation of CrN into Cr₂N, while after annealing in air, only Cr₂O₃ phase was observed.

Safi (2000) investigated the influence of d.c. reactive sputtering conditions such as hysteresis effect and instability in the gas pressure, differential poisoning of target during deposition of thin films. The sputtering process was controlled effectively by higher pumping speed, increasing target to substrate distance, obstructing the reactive gas flow to the target, pulsed reactive gas flow, plasma emission monitoring, and voltage control. Nam *et al* (2000) studied the influence of high deposition rate in magnetron sputtering to control the microstructures of CrN thin films. They found that deposition of CrN com-

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pound has increased up to 90% than pure Cr coating due to increase in ionization efficiency upon applying negative pulsed d.c. bias voltage. Cunha *et al* (1999) studied the CrN films produced by d.c. and RF reactive magnetron sputtering on SA316 substrate and found that the average density of the coatings varies between 55 and 85% of the bulk density and it affects the mechanical properties of the coatings.

Barshilia *et al* (2006) investigated the unbalanced magnetron pulsed d.c. sputtered CrN hard coatings and reported that the film hardness is affected by several factors such as packing factor, residual stress, stoichiometry, preferred orientation, and grain size. They have also investigated the effect of high temperature on CrN and CrAlN coatings deposited by d.c. magnetron sputtering on mild steel and silicon substrate and reported that the oxidation of CrN coating has occurred around 600°C but no detectable oxides were formed on CrAlN coating even at 800°C (Barshilia *et al* 2006a).

The application of bias has no effect on the phase formation but it influences the preferred crystal orientation and the residual tensions in d.c. magnetron sputtered CrN thin films (Forniés *et al* 2006). Geun *et al* (2006) observed that the tribological property of CrN deposited by cathodic arc ion plating (CAIP) is dependent on the combined effect of textures, surface roughness, residual stress, and surface hardness of the films. Also, sputter deposited CrN films with high residual stresses affects the film–substrate interface adhesion; while it improves the erosion resistance of the brittle materials (Mariusz and Dongyi 2005). The residual stresses in thin films are due to low deposition temperature, working gas entrapment, and surface tension forces at the film/substrate interface (Ohring *et al* 2006).

The literature on influence of process parameters in the reactive magnetron sputtering technique on the microstructural characteristics of CrN thin films is very limited. It is very essential to substantiate the role of different sputtering conditions for achieving the desired microstructural characteristics in the CrN thin films with enhanced tribological properties. Therefore, the present work has been focused to study the microstructural features of the CrN thin films, deposited by d.c.-reactive magnetron sputtering, as a function of sputtering conditions such as substrate temperature, gas pressure, and power. An accurate control of stoichiometry and composition is possible in d.c.-reactive magnetron sputtering as compared to RF system.

The effects of process parameters on the microstructural characteristics of the CrN thin films such as phase formation, grain morphology, textures, and surface roughness were investigated by techniques such as XRD, AFM, and FE-SEM in the present work. Microhardness tester was used to measure the hardness of CrN thin films deposited on stainless steel substrate and the deformation characteristics of the films are explained using its microstructural features.

2. Experimental

2.1 Deposition of CrN films

The stainless steel substrate SS304 with a dimension of $10 \times 10 \times 0.9$ mm was prepared for the deposition of CrN thin films using d.c. reactive magnetron sputtering. Prior to the deposition, stainless steel (SA-304) samples were mechanically polished up to $0.3 \mu\text{m}$ using Fe_2O_3 powder in distilled water. Thereafter, the samples were ultrasonically cleaned in water bath for 15 min followed by rinsing in acetone solution. The environment in the sputtering chamber was a mixture of Ar + N_2 gases. The base pressure was in the range of 4×10^{-6} Torr before the gases such as Ar and N_2 were allowed to enter the chamber. A Cr (99.99% purity) target of 50 mm in diameter was used during the sputter deposition. The gas ratio, base pressure, substrate to target distance and deposition time were held constant, during deposition, while temperature, working pressure and power were set to different values. The deposition parameters are summarized in table 1.

2.2 Characterization

2.2a XRD characterization: The phases and their preferred orientation of CrN thin films were characterized by X-ray diffraction (Bruker AXS, D8 Advance). The basic structural properties of films in the as deposited condition were determined by $\theta/2\theta$ scans with $\text{CuK}\alpha$ radiation ($\lambda = 0.15418$ nm) in the range of 30° to 100° to find the possible changes in the texture orientation. The scan rate was $1^\circ/\text{min}$ with an increment of 0.05° . The excitation voltage and current were set to 40 kV and 30 mA, respectively, in the diffractometer. For each (*hkl*) plane, full width at half maximum (FWHM) was determined and from this value, the grain size of films was calculated using the Scherrer formula (Cullity *et al* 1977)

$$D = \frac{0.9\lambda}{\text{FWHM} \cos \theta}, \quad (1)$$

where D is the grain size along the surface normal direction, λ the X-ray wavelength, θ the Bragg angle and

Table 1. Sputtering deposition parameters.

Sr. no.	Deposition parameters	Values
1	Pulsing parameters	d.c.
2	Base pressure	$\leq 4 \times 10^{-6}$ Torr
3	Working pressure	10, 15, 20 mTorr
4	Temperature	200°C, 300°C, 400°C
5	Target to substrate distance	50 mm
6	Deposition environment	Ar + N_2
7	Deposition time	60 min
8	Target power	75 W, 100 W
9	Gas ratio	50 : 50

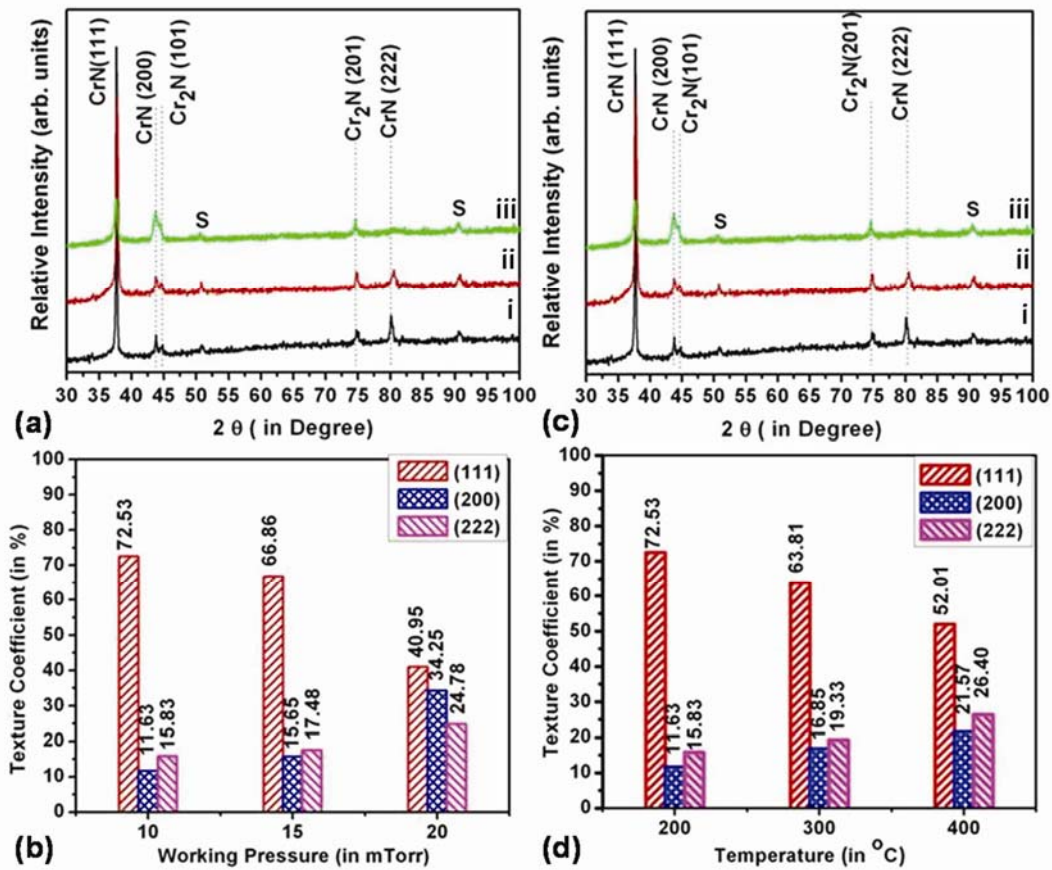


Figure 1. XRD peaks and texture coefficient of CrN films deposited on SS-304 substrate: (a) and (b) as a function of working pressure: (i) 10 mTorr, (ii) 15 mTorr, (iii) 20 mTorr, deposited at 200°C, while (c) and (d) as a function of temperature: (i) 200°C, (ii) 300°C and (iii) 400°C deposited at 10 mTorr.

FWHM the corrected full width at half maxima. The grain size is inversely related to the FWHM of the diffraction peak as shown in (1). The larger grain size exhibits a narrow peak, which is due to the periodicity of the individual grain domains which are in phase, reinforcing the X-ray beam.

2.2b FESEM and AFM characterization: The morphologies of CrN film surface in as deposited conditions were characterized by FE-SEM (FEI, Quanta 200F) and atomic force microscopy (AFM, NT-MDT) and its chemical composition was measured using energy dispersive spectroscopy (EDS). The microhardness of CrN/SS was measured using microhardness tester.

3. Results and discussion

3.1 Texture and crystallite size of films

The effect of working pressure and temperature on XRD peak intensity of CrN thin films deposited on the stainless steel SA-304 substrate in Ar + N₂ chamber, while keep-

ing remaining parameters constant is shown in figures 1a and c. The films exhibit (111) preferred orientation and it changes with working pressure and temperature. It is found that the dominant (111) orientation becomes a preferred orientation even with increase in working pressure. It is due to narrow lower range selection of working pressure in the present study. However, during the initial time of lower working pressure, a mixture of (111), (200) and (222) orientations (compared to the values d_0 reported in JCPDS 76-2494 card) with 72.53%, 11.63% and 15.85%, respectively was observed. However, at the higher working pressure, (200) and (222) preferred orientations have increased among the (111), (200) and (222) orientations; while (111) intensity is reduced. Also, at low working pressure, (101) and (201) orientations of Cr₂N phase were observed and (101) phase of Cr₂N transforms into (111) phase of CrN phase at higher working pressure and temperature. The formation of (101) and (201) orientations could be due to higher surface free energies of substrate material and higher N₂ content in the sputtering chamber. The texture coefficient (Chawla *et al* 2008) of the CrN film as a function of working pressure and temperature

Table 2. Average crystallite size using XRD peaks and AFM, thickness, deposition rate and stresses developed at different working pressure and temperature.

CrN sample no.	Temperature (°C) and power (W)	Working pressure (mTorr)	Crystallite size (nm)		Average film thickness (nm)	Deposition rate (nm/min)	Stresses (GPa)
			XRD	AFM			
1	200°C, 75 W	10	34.59	31.41	2220	37.00	0.68
2		15	25.95	35.29	2040	34.00	1.49
3		20	18.86	24.10	1940	32.33	-0.10
4	200°C, 100 W	10	27.68	101.92	3630	60.50	-1.77
5		15	37.72	90.23	3310	55.16	-0.81
6		20	31.90	116.13	3080	51.33	1.02
10	300°C, 75 W	10	34.58	54.33	2080	34.66	-0.55
11		15	37.73	32.80	2370	39.50	0.36
12		20	44.44	123.92	2650	44.16	-1.64
13	300°C, 100 W	10	29.62	48.21	3510	58.50	-1.80
14		15	37.70	73.44	3560	59.33	-1.82
15		20	34.56	*412.33	3240	54.00	-1.62
19	400°C, 75 W	10	31.91	64.95	1960	32.66	-0.81
20		15	31.91	95.81	2560	42.66	-1.81
21		20	25.93	90.56	3440	57.33	-0.68
22	400°C, 100 W	10	37.72	80.40	2960	49.33	-0.41
23		15	29.62	60.55	3310	55.16	-1.46
24		20	31.90	70.42	3560	59.33	-1.50

*Indicates crystallite size with few several hundred nm size.

are calculated using (2) and the results are shown in figures 1b and d, respectively

$$T = \frac{I_{hkl}}{I_{222} + I_{200} + I_{111}}, \quad (2)$$

where hkl represents the (111), (200) or (222) orientations of the films.

The texture coefficient is affected by the working pressure and temperature during deposition. The (111) orientation transforms into (200) orientation at higher value of working pressure. The combined effect of working pressure and power indicated that pressure rendered a greater effect on stress induced in the film deposited at low power than the deposited films at higher power. Intrinsic stress in the films increases (from compressive to tensile) linearly and it remains constant even after deposition, called low mobility Volmer–Weber growth, which increases at higher temperature (Ohring 2006). The changes in the preferred orientation of CrN thin films are due to the following reasons. The deposition rate decreases with increase in sputtering pressure owing to the reduction of mean free path (MFP). With the increase in working pressure, more collision of sputtered particles occurs when the particles move from target to substrate and due to the frequent collisions, some of the sputtered particles are back scattered and therefore, it reduces the deposition rate. Hence, the reduction in deposition rate with increasing working pressure influences the crystallinity, texture, and the porosity of as deposited thin films.

It is evident that the peak intensity of (111) orientation is decreasing with increasing value of working pressure and temperature as shown in figure 1(b and d).

The interplanar spacing, d -value of the film, is calculated using Bragg's relation from the position of the (111) peak. The observed d -value at 10 mTorr working pressure with keeping other parameters constant (200°C and 75 W), initially decreases with increase in working pressure, due to high compressive residual stresses induced in the film during deposition. After 15 mTorr value of working pressure, the increase in d -value is due to tensile stresses in the deposited films. The grain size and FWHM of CrN thin films is calculated and plotted against working pressure as shown in figure 2. It is observed that the grain size of (111) peak decreases with increase in working pressure. The grain size reduces with working pressure, while keeping temperature (200°C) and power (75 W) constant, as shown in table 2. The reduction in grain size is mainly due to higher proportion of nitrogen content, which increases the mean free path causing less number of collisions with gas particles in the chamber. The sputtered Cr atoms also undergo less collisions leading to a low probability of agglomeration and growth even before arriving at the substrate (Chandra *et al* 2006).

3.2 Morphology of CrN thin films

A pyramid shaped topographical growth and columnar morphology of the films were observed at different working pressures as shown in cross sectional SEM images of

CrN (figure 3). The rate of deposition was restricted with increasing working pressure. The thickness of CrN films deposited at different working pressures is shown in table 2. A limiting crystallite size of the thin films has been identified in the grain refinement process. The crystallite size of the films deposited at 10, 15 and 20 mTorr working pressure and with power of 75 W, was 34.59, 25.95 and 18.86 nm, respectively. The rate of reduction of crystallite size was found to be slower due to highly textured grains in the film and the narrow range of working pressure. The highly textured grains indicate that the strain energy is higher in the films and the grains are heavily dense.

The surface morphologies of the as deposited CrN coatings were studied using AFM. The 3D surface morphologies of CrN coatings are shown in figure 4. The root mean square (RMS) roughness values of the as-deposited CrN coatings were calculated and their values at 200°C temperature were 7.69 nm, 7.79 nm, and 3.02 nm for 10, 15 and 20 mTorr pressure, respectively. However, with the increasing temperature (200°C, 300°C and 400°C) at the same working pressure (10 mTorr), the RMS values were 7.69, 14.31 and 20.65 nm. The increasing deposition temperature affects the grain size as evident from the results of AFM and XRD. The higher grain size of the CrN coating at higher temperature may be due to increased diffusivity of atoms facilitating the grain growth. The mobility of grain boundaries leads to variations in the surface topography and morphology of the CrN coatings as observed from its AFM images.

3.3 Residual stress

The thin films developed by physical vapour deposition techniques normally contain internal or residual stress

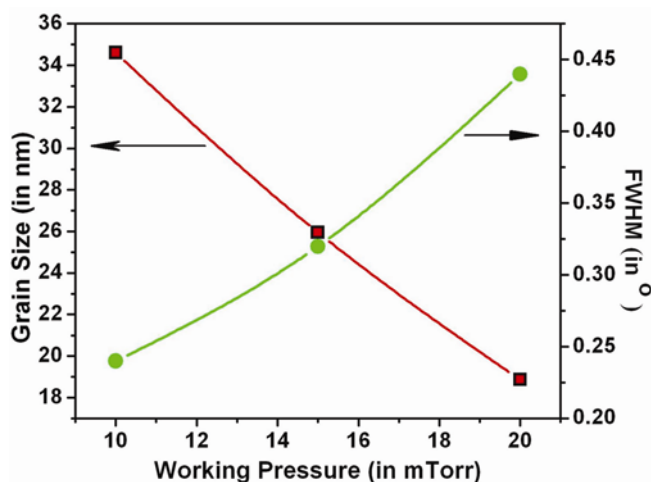


Figure 2. The dependence of the grain size and FWHM on the working pressure of CrN films deposited at 200°C and power, 75 W.

within it. The magnitude of residual stress present in thin films affects its properties, particularly adhesion and

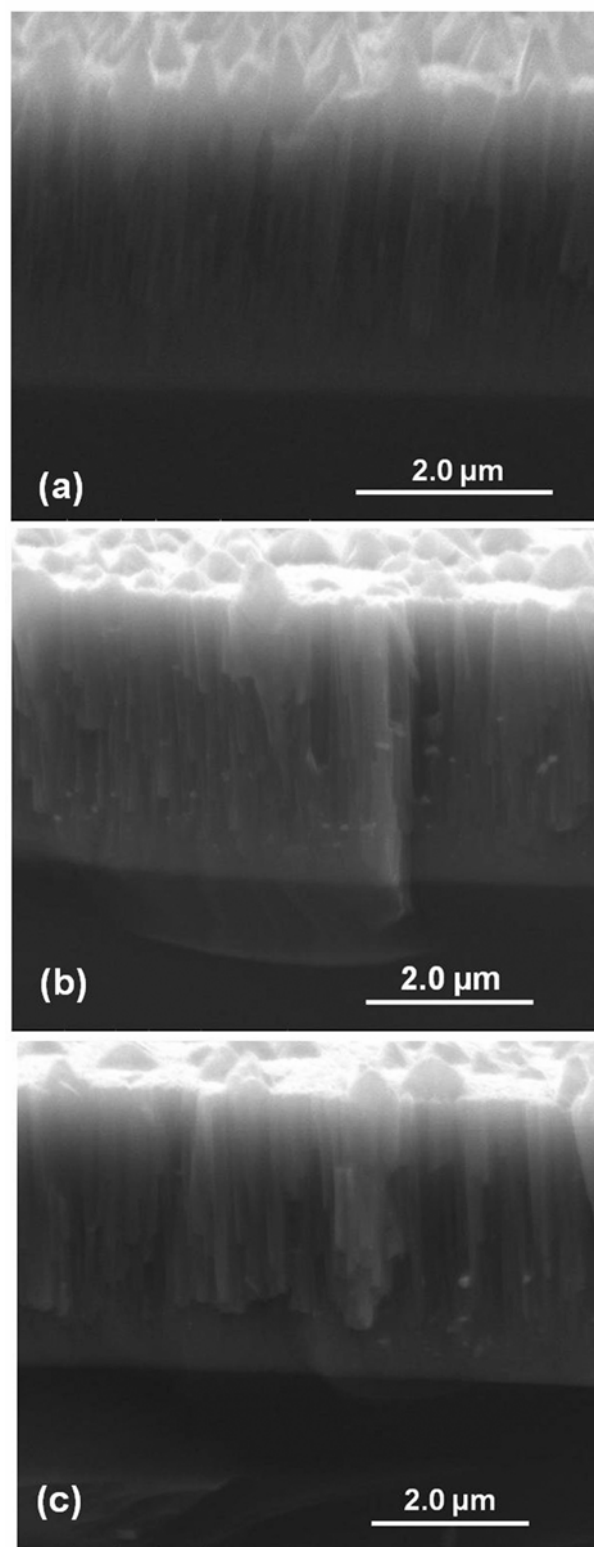


Figure 3. Scanning electron micrographs of fracture cross sections of CrN thin films deposited at different working pressure and temperature.

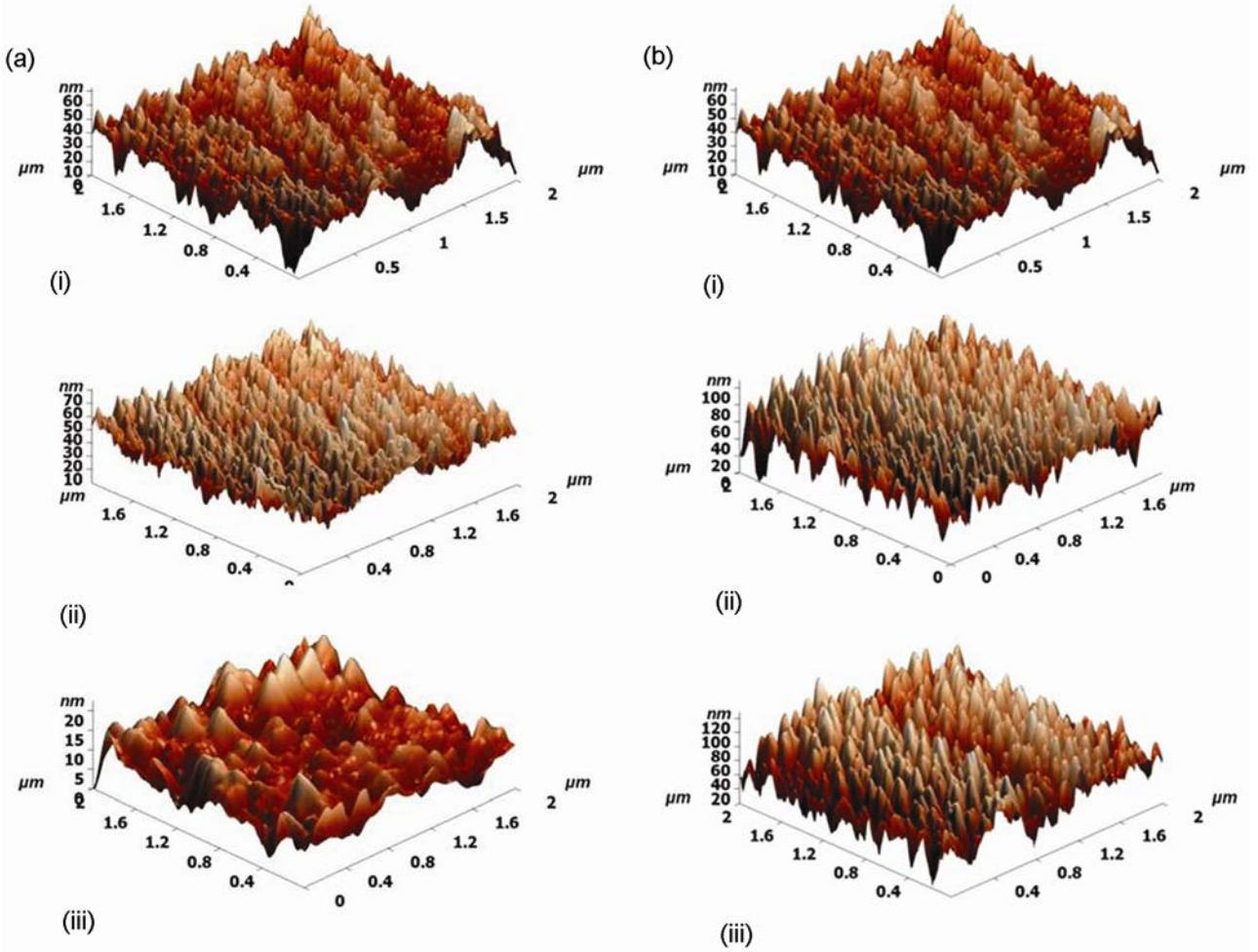


Figure 4. AFM surface morphologies of CrN thin films: (a) as a function of working pressure deposited at 200°C: (i) 10 mTorr, (ii) 15 mTorr and (iii) 20 mTorr and (b) as a function of temperature deposited at 10 mTorr pressure: (i) 200°C, (ii) 300°C and (iii) 400°C.

mechanical properties. The residual stress induced in the films is controlled by the various process parameters at the time of deposition. The biaxial stress (σ_{xy}) in the CrN thin films is calculated using (3)

$$\sigma_{xy} = -\frac{1}{\nu}(E\varepsilon_z - \sigma_z), \quad (3)$$

where ε_z along the direction z perpendicular to the $X-Y$ plane given by

$$\varepsilon_z = \frac{(d_{hkl} - d_0)}{d_0}, \quad (4)$$

and E is Young's modulus of film (245 GPa), ν is Poisson ratio of film (0.23) (Lamastra *et al* 2006), d_{hkl} the spacing between two planes in stressed condition (during deposition), d_0 the standard interplanar spacing in unstressed condition of CrN thin film, and σ_z the stress in z direction (perpendicular to substrate) is zero assuming a biaxial stress condition. It is evident from the stress analysis of CrN films that the stresses are reduced with

the increase in working pressure and temperature as shown in table 2. It has been reported in the literature (Fabis *et al* 1990) that the average stress deposited in CrN films is affected mainly by three parameters: sputtered flux incidence angle, sputtering pressure, and film thickness. In d.c. reactive sputtering deposition technique, increasing the working pressure ($\text{Ar} + \text{N}_2$) reduces the intrinsic stress generated in the film because of mainly two reasons: the reduction in energies of plasma particles due to inelastic scattering of gas and a decrease in discharge voltage at fixed current with increasing working pressure. Similarly, power density also affects the intrinsic stress of the CrN film by influencing the effect of other deposition parameters.

3.4 Microhardness

The hardness of CrN films was measured by an optical microhardness tester (Model: Miniload-II, Mfg: Leitz, Germany) with Vickers indentation tip. The indenter tip

is made up of diamond with pyramid shape, its square sides with opposite faces, edges, and face angles are at an angle of 136°, 148°, and 68°, respectively. Vicker's diamond hardness (VDH) is calculated using (5) with the input of the indenter load and the actual surface area of the impression

$$VDH = 1.8544 \frac{P}{d^2} \quad (5)$$

The applied load value was 20 g with 28 s loading time. The indentation was made on five different points in each CrN/SS sample to obtain its average hardness value. The calculated hardness is given in tables 3a and b. It is observed that the CrN film deposited at 200°C (with 75 W power), its hardness has reduced from 1030 ± 23 to 856 ± 21 Hv with increase in working pressure from 10–20 mTorr. It is because of the presence of crystal imperfection during film growth at increased working pressure and low temperature. However, the hardness of films increases slightly from 1030 ± 23 to 1226 ± 24 Hv with increase in deposition temperature to 400°C for same working pressure. The increase in the hardness may be due to grain refinement (from 34.59 to 18.86 nm) (Mayrhofer *et al* 2001). On the other hand, the effect of power showed that the CrN film deposited at 100 W, showed an increase in hardness value from 1371 ± 16 Hv

to a maximum of 1831 ± 27 Hv for the temperature and working pressure of 400°C and 10 to 20 mTorr, respectively. The microhardness of the films increases with increase in substrate temperature, T_s , as reported in the literature (Gautier *et al* 1996). With increasing T_s , the mobility of atoms increased leading to a more perfect structure. The hardness values of CrN thin films measured in the present work are in tandem with that of the reported hardness value of 1800 Hv, which is higher than of its bulk CrN (1100 Hv) (Hones *et al* 1997). The hardness of conventional metallic material can be well described by Marsh relations (Marsh 1964), which takes into account the elastic modulus, E , Poisson ratio, ν and yield strength. Normally, the maximum theoretical strength of a solid is a function of the strength of interatomic bonds between atoms and is given by $E/10$ (Kelly and Macmillan 1986), which comes to around 32 GPa (obtained using Vicker's indentation and Marsh relation) for CrN films ($E = 245$ GPa and $\nu = 0.23$). However, in actual practice, it is never observed due to the presence of crystal imperfections and defects in the form of cracks present in the films.

Table 3. (a) Hardness values of CrN films deposited at 75 W.

CrN sample no.	Temperature (°C) and working pressure (w)	Hardness (Hv)
1	200°C, 10	1030
2	15	891
3	20	856
10	300°C, 10	990
11	15	1226
12	20	1393
19	400°C, 10	1226
20	15	1174
21	20	1158

Table 3. (b) Hardness values of CrN films deposited at 100 W.

CrN sample no.	Temperature (°C) and working pressure (w)	Hardness (Hv)
4	200°C, 10	1483
5	15	952
6	20	757
13	300°C, 10	1371
14	15	1426
15	20	1679
22	400°C, 10	1371
23	15	1483
24	20	1831

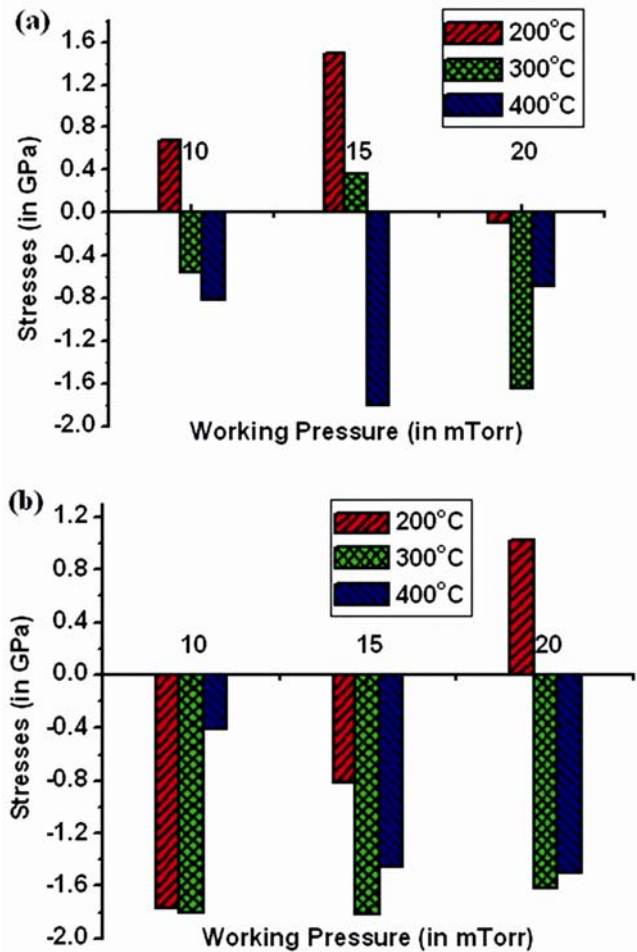


Figure 5. Intrinsic stresses produced in CrN films deposited at (a) 75 W and (b) 100 W.

The strength and hardness of bulk material can be increased by increasing its dislocation density during plastic deformation. The hardness increases due to reduction in grain size and higher volume fraction of grain boundaries, which contributes for the accumulation of immobile dislocation density in the materials. The minimum stresses required to activate dislocation sources will increase with reduction in particle size to nano phase (Mayrhofer *et al* 2006). The similar mechanisms may be applicable to strengthening of thin films in addition to the role of residual stress and substrate effect.

4. Conclusions

The CrN films deposited on stainless steel substrates by reactive magnetron sputtering process has been investigated in the present work. The effect of working pressure, temperature and power on the microstructural characteristics such as texture, grain morphology, and surface roughness of CrN films has been analysed. The experimental results have shown that CrN films exhibit at (111) preferred orientation and it transforms into (200) orientation with increasing working pressure. The film exhibits a higher crystallinity with large grain size at lower working pressure. The preferred orientations of the CrN films depend on sputtering conditions, thickness of the films, and the induced residual stress in the thin films as observed in the present work. The microhardness of CrN thin films was measured and it showed an increasing trend with increase in combined effect of temperature, working pressure, and power density. The higher hardness of the films is due to the grain size effect, highly textured grains and compressive residual stress in the films.

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