The structure and properties of chromium nitride coatings deposited using dc, pulsed dc and modulated pulse power magnetron sputtering

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The time averaged ion energy distributions and ion fluxes of continuous dc magnetron sputtering (dcMS), middle frequency pulsed dc magnetron sputtering (PMS), and modulated pulse power (MPP) magnetron sputtering plasmas were compared during sputtering of a Cr target in an Ar/N₂ atmosphere in a closed field unbalanced magnetron sputtering system. The results showed that the dcMS plasma exhibited a low ion energy and ion flux; the PMS plasma generated a moderate ion flux of multiple high ion energy regions; while the MPP plasma exhibited a significantly increased number of target Cr⁺ and gas ions with a low ion energy as compared to the dcMS and PMS plasmas. Cubic CrN coatings were deposited using these three techniques with a floating substrate bias. The structure and properties of the coatings were characterized using X-ray diffraction, scanning electron microscopy, transmission electron microscopy, nanoindentation, microscratch and ball-on-disk wear tests. It was found that the deposition rate of the MPP CrN depositions was slightly lower than those of the dcMS depositions, but higher than in the PMS depositions at similar average target powers. The coatings deposited in the dcMS and PMS conditions without the aid of the substrate bias exhibited large columnar grains with clear grain boundaries. On the other hand, the interruption of the large columnar grain growth accompanied with the renucleation and growth of the grains was revealed in the MPP CrN coatings. The MPP CrN coatings exhibited a dense microstructure, fine grain size and smooth surface with high hardness (24.5 and 26 GPa), improved wear resistance (COF = 0.33 and 0.36) and adhesion, which are the results of the low ion energy and high ion flux bombardment from the MPP plasma.

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1. Introduction

The structure and properties of the films can be usefully modified by means of suitably controlling the energy and flux of ion impingement on the substrate surface in ion or plasma assisted deposition processes. The ion bombardment on the growing film provides incident atoms with additional energies, which can modify the nucleation process, increase the film density, and change the texture, stress and microstructure of the films [1–5]. The ion energy and ion to neutral ratio are critical for controlling the structure and properties of the sputtered films. Petrov et al. [1] showed the effects of different ion to neutral ratios of the arriving species at the substrate as a function of the ion energy on the structure and properties of the TiN films. For films deposited under a low ion flux and ion energy condition, the structure of the films was porous. As the ion energy was increased at the low ion flux condition, the density of the films increased, but the effect of the higher energy conditions led to damage of the microstructure of the film, which could be annealed out by the thermal energy input. However, when there was a high ion to neutral ratio but with a low ion energy (<20 eV), it was possible to deposit fully dense films. In addition, these films exhibited a lower defect density and lower residual stresses as compared to films deposited under low flux high energy ion irradiation.

The ion energy and ion to neutral ratio within the plasma are strongly dependent on the sputtering technique. In general, the ion energy and ion flux are low in the continuous dc magnetron sputtering (dcMS) plasma. In the middle frequency bipolar pulsed dc magnetron sputtering (PMS), as the target voltage is rapidly switched between positive and negative values in either asymmetric or symmetric modes, the reversed positive voltage during the pulses significantly changes the plasma properties, e.g. ion energy, ion flux, electron density and temperature. A wide range of ion energy distributions in the PMS plasma (up to hundreds of eV) has been reported [6–10]. However, these pulsed ion energies, which are strongly dependent on the target material and the pulsing parameters, need to be carefully controlled to avoid excessive ion bombardment [11]. In recent years, the development of the high-power pulsed magnetron sputtering (HPPMS) (also called high-power impulse magnetron sputtering (HIPMS)) [12–15] and the alternative technique named modulated pulse power (MPP) sputtering [16–21],...
have broadened the operating window for the magnetron sputtering. By applying a large amount of peak power and current to a target (e.g. 0.1–3 kW/cm²) for a short period of time (e.g. in the μs to ms range), the HPPMS/HIPIMS and MPP techniques can produce a high degree of ionization of the target material and a high plasma density. Nevertheless by pulsing the power, the average target power remains as low as in the dcMS and PMS conditions to avoid overheating of the target. Therefore, it is possible to achieve extremely high ion to neutral ratios in the HPPMS/MPP plasmas that can be utilized to improve the structure and properties of the films. As a unique HIPIMS technique, the MPP process uses longer pulse lengths in the 1–3 ms range compared to the 100–150 μs range for HPPMS. The MPP process can also arbitrarily modify the pulse shape to achieve different ionization stages and a stable discharge for different target materials. For detailed descriptions of the MPP technique, the readers are referred to refs [20,21].

Chromium nitride (CrN) coating is an important hard transition metal nitride coating that exhibits good hardness, wear resistance and high corrosion resistance [22–26]. DcMS and mid-frequency PMS are well-established methods for the reactive magnetron sputtering of CrN coatings. Lin et al. [26] compared the structure and properties of CrN coatings deposited at different Ar/N₂ flow ratios using dcMS and PMS in a closed field unbalanced magnetron sputtering (CFUBMS) system. They showed that the CrN coating deposited by PMS exhibited an improved microstructure and properties due to the enhanced energetic ion bombardment in the PMS plasma. It has also been demonstrated recently that the highly ionized plasma generated by HIPIMS/HPPMS technique can be usefully utilized to tailor the microstructure and properties of magnetron sputtered CrN coatings [27–29]. Ehiasarian et al. [27] used the HIPIMS technique to deposit high density and droplet free CrN coatings with excellent adhesion, high hardness (HK0.025 = 2600) and low coefficient of friction (0.4). Alami et al. [29] showed that the morphology of CrN coatings changed from a porous columnar structure for the dcMS films to a dense and featureless morphology for the HPPMS films deposited at a peak target current of 180 A. However until now, there have been few detailed reports on the reactive sputtering CrN coatings using the MPP technique.

In this study, CrN coatings were deposited using three sputtering techniques (dcMS, PMS and MPP) by sputtering a Cr metal target in an Ar/N₂ mixture in a CFUBMS system. A floating substrate bias was used for all depositions to ensure that the kinetic energy of the ion bombardment on the growing film was mainly from the intrinsic plasma. The ion energy distributions (IED) of the plasma generated by these techniques were measured using a Hiden Electrostatic Quadrupole Plasma Mass Spectrometer (EQP) in an effort to understand the correlation between the plasma properties generated in these magnetron sputtering techniques and the resultant structure and properties of the deposited CrN coatings.

2. Experimental details

The deposition system is a cylindrical chamber equipped with two unbalanced magnetrons (Teer, Coatings LTD.) of reversed magnetic polarities, which were placed opposite one another at a distance of 240 mm to form a closed magnetic field, as illustrated in Fig. 1. The substrates (304 stainless steel coupons and Si (100) wafers) were ultrasonically cleaned in acetone and alcohol successively, and blown dry with N₂. The distance between the Cr target and the substrate holder was 140 mm. The target size was 300 mm × 100 mm. The chamber was pumped down to a base pressure under 1.33 × 10⁻⁵ Pa prior to the depositions. The substrate surface was sputter etched by Ar ion bombardment at a 1.34 Pa working pressure with a ~ 400 V pulsed dc bias (100 kHz and 90% duty cycle) for 30 min. A 150–200 nm Cr adhesion layer and the following CrN coatings were deposited by sputtering of the metal Cr target in an Ar and Ar/N₂ mixture respectively, using continuous dc (Pinnacle, Advanced Energy Inc.), middle frequency pulsed dc (Pinnacle Plus, Advanced Energy Inc.) and MPP (SOLO/AXIS-180™ Pulsed DC Plasma Generator, 2pulsar LLC.) power sources. During the depositions, high purity Ar and N₂ (99.999%) were introduced into the system separately using MKS mass flow controllers. The working pressure, which was measured by a high precision capacitance manometer, was kept constant at 0.67 Pa by balancing the pumping speed and the total gas flow rate (52 sccm). The Ar:N₂ gas flow ratio was maintained at 1:1.

In the dcMS and PMS conditions, an average target power of 1 kW was used. For the PMS depositions, an asymmetric bipolar pulsed voltage was applied on the Cr target with the pulsing parameters of 100 kHz and 60% duty cycle (the target voltage was reversed to 10% of the nominal negative sputtering voltage during the positive pulse period). Two pulse shapes were used in the MPP depositions as shown in Fig. 2. The solid lines represent the waveforms for the MPP-1 pulse, and the dashed lines represent the waveforms for the MPP-2 pulse. The total pulse width for the two pulses was 1500 μs, which started with a 500 μs weak ionization stage and then was ramped up to a strong ionization stage. The pulsing frequency was set at 30 Hz for both conditions. However different peak powers and peak currents during the high ionization stage lead to an average target power (Pₜ) of 1 kW and 4 kW in the MPP-1 and MPP-2 conditions, respectively, as
summarized in Table 1. A floating substrate bias was used for all coating depositions.

A Hiden Analytical Ltd EQP was used to characterize the time averaged IEDs in the dcMS, PMS and MPP plasmas. The EQP probe was installed parallel to the target surface through the side of the chamber. The EQP axis was placed exactly along the middle line between two targets. The distances between the EQP oriﬁce (100 µm) to the target surfaces and the center of the chamber were 120 and 25 mm respectively, as shown in Fig. 1. The ion energies measured by the EQP are the plasma potential relative to the ground potential. During the plasma examination, a negative voltage of $-20$ V was applied on the filament for attracting and sampling the positive ions within the plasma. The IED scans were measured from $-5$ to $100$ V with a step size of 0.5 V and a 100 ms dwell time. The same tuning parameters for the spectrometer were applied for all measurements.

The crystal structure of the coatings was characterized by a Siemens X-ray diffractometer (Model KRISTALLOFLEX-810) operated at 30 kV and 20 mA in the $\theta$–$2\theta$ mode. The grain size of the coatings ($t$) was estimated from the (200) diffraction peak using the Scherrer equation [30],

$$\lambda = 0.9 \frac{\lambda}{(B \cos \theta)} \quad (1)$$

where $\lambda$ is the X-ray wavelength (0.15406 nm for Cu), $\theta$ is the Bragg angle of the diffraction peak, and $B$ is the full-width-half-maximum (FWHM) of the peak.
surface morphology and cross-sectional microstructure of CrN coatings were characterized using a JSM-7000F field-emission scanning electron microscope (FESEM) operated at a 5 kV accelerating voltage. Cross-sectional TEM samples were prepared by gluing two coated Si wafers face to face into a ‘sandwich’, which was polished down to 20–30 μm using the conventional ‘tripod’ grinding method followed by Ar⁺ ion milling to electron transparency (Gatan Duoo-mill). A Philips/FEI CM200 transmission electron microscope (TEM) operated at 200 kV was used to examine the coating microstructure.

The hardness and Young’s modulus of the coatings were measured by an MTS nano-indentor XPPII equipped with a Berkovich diamond indenter. The calculations were made by the Oliver and Pharr method from the load–displacement curve using 10% of the coating thickness as the indentation depth [32]. A microscratch tester (CSM instrument, LLC) was used to evaluate the adhesion strength of the coatings using a Rockwell C indent tip (200 μm). The applied load was increased from 0.03 N up to 30 N with an increasing load of 0.5 N/s. The scratch tests were examined by the attached optical microscope to identify the coating failure morphologies with the critical loads. The wear resistance of the coatings was evaluated by a ball-on-disk microtribometer (Center for Tribology, Inc) in an ambient atmosphere (a relative humidity of 25 ± 1 RH% and a temperature of 25 ± 1 °C) by sliding against a 1 mm WC-Co ball at a velocity of 25 mm/s for a 150 m sliding distance. The normal load applied on the sample surface was 3 ± 0.2 N which was controlled by a load suspension system. The average coefficient of friction (COF) values were read from the steady sliding state during the tests. After the wear tests, the wear tracks were examined using a Veeco 3D surface profilometer to measure the wear volume and calculate the wear rates.

3. Results and discussions

3.1. Ion energy distributions and ion flux

The Cr⁺, Ar⁺ and N₂⁺ IED curves measured during sputtering of a metal Cr target in an Ar: N₂=1:1 atmosphere using dcMS, PMS and MPP power sources are shown in Fig. 3a,b and c respectively. The IED curves were also plotted with a logarithmic scale and inserted in the figures for the illustration of the existence of ions in the high energy range. Fig. 3d depicts the integrated areas under the IED curves, which are relevant to the number of ions (ion flux). As summarized in Table 1, the Pp was 1.0 kW for the dcMS, PMS and MPP-1 conditions, whereas the Pp was 4 kW in the MPP-2 condition. The peak power (Pp) was 49 and 180 kW, and the peak current (Ip) was 100 and 250 A in the MPP-1 and MPP-2 conditions, respectively.

The IEDs of dcMS Cr⁺, Ar⁺ and N₂⁺ ions (the solid box symbols) exhibit a peak energy of 4 eV and a maximum ion energy of 15 eV in the tail (Fig. 3a, b and c). The integrated ion fluxes in dcMS condition are low (Fig. 3d). The numbers of Ar⁺ and N₂⁺ ions are much higher than that of Cr⁺ ions, suggesting that the major ion species in the dcMS plasma is from the gas, while the ionization degree of the metal target species is low.

Table 2

The mechanical and tribological properties of dcMS, PMS and MPP CrN coatings deposited using a floating substrate bias.

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<tbody>
<tr>
<td>dcMS</td>
<td>0.98</td>
<td>105</td>
<td>-0.9</td>
<td>27.5</td>
<td>16.0</td>
<td>280</td>
<td>0.057</td>
<td>0.58</td>
<td>8.75</td>
</tr>
<tr>
<td>PMS</td>
<td>0.94</td>
<td>78</td>
<td>-2.0</td>
<td>17.4</td>
<td>21.0</td>
<td>256</td>
<td>0.082</td>
<td>0.45</td>
<td>3.65</td>
</tr>
<tr>
<td>MPP-1</td>
<td>0.94</td>
<td>45</td>
<td>-1.4</td>
<td>5.7</td>
<td>24.5</td>
<td>268</td>
<td>0.086</td>
<td>0.36</td>
<td>2.43</td>
</tr>
<tr>
<td>MPP-2</td>
<td>0.96</td>
<td>60</td>
<td>-1.2</td>
<td>8.2</td>
<td>26.0</td>
<td>310</td>
<td>0.084</td>
<td>0.33</td>
<td>2.40</td>
</tr>
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* Lc1: Semi-circular coating cracks inside the scratch track.
* Lc2: Adhesive chipping at track edges.
* Lc3: Initial failure of coating.
* Lc4: Total failure of coating (substrate completely exposed).
When the target was pulsed at 100 kHz and 60% duty cycle in the PMS condition, a wide range of ion energies was observed in the plasma (the open cycle symbols), which contains two energy peaks as depicted in Fig. 3a to c. The first peak is the low energy region with a peak energy at 3 eV, which was generated during the negative dc sputtering period in the pulses. The second energy peak is a high energy region with ion energies in a range of 30 to 50 eV, which is the energy gained during the reversed pulse period as the target voltage is switched to the positive values of about 10% of the negative sputtering voltage [10,11]. In addition to these two major ion energy peaks, there is a small number of ions with a wide energy distribution extended above 100 eV (as identified in the curves plotted with the logarithmic scale). An increase in the numbers of Cr⁺, Ar⁺ and N₂⁺ ions was identified in the PMS plasma as compared to the

Fig. 6. The cross-sectional and top view SEM micrographs of CrN coatings deposited under (a) and (b) dcMS, (c) and (d) PMS (100 kHz and 60% duty cycle), (e) and (f) MPP-1 (Pp = 49 kW and Ip = 100 A), and (g) and (h) MPP-2 (Pp = 180 kW and Ip = 250 A) conditions at a floating substrate bias.
dcMS condition, as shown in Fig. 3d. However, similar to the dcMS condition, it can be seen that the ionization degree of the target metal species is still low as compared to the gas ion species in the PMS plasma.

As shown in Fig. 3a to c, the MPP plasma exhibited a peak ion energy of 4 eV which is similar to the dcMS condition in the Ar/N₂ mixture. However, the maximum ion energy in the tail increases to a value of 22 and 30 eV for the MPP-1 (P₀ = 1 kW) and MPP-2 (P₀ = 4 kW) conditions respectively. Unlike in the PMS condition, no higher energetic ions can be observed in the MPP conditions. Nevertheless, the integrated ion fluxes of all ion species increased as compared to the dcMS and PMS conditions (Fig. 3d). Moreover, the intensity of the Cr⁺ ion flux is higher than those of the gas ions, and increased significantly as the average target power was increased. This observation confirmed that a large number of target metal atoms were ionized in the MPP plasma by the high peak power and current applied on the target. Similar observations of high ionization degree of the target material in HPPMS/HIPIMS plasmas have also been widely reported [13–15,33].

In a short summary, the dcMS plasma exhibited a low ion energy and ion flux; the PMS plasma exhibited a wide range of ion energies (can be up to hundreds of eV) and a moderate ion flux; and the MPP plasma exhibited a low ion energy but an extensive ion flux, especially for the metal ions.

### 3.2. Deposition rate and microstructure of the CrN coatings

Fig. 4 shows the deposition rates for dcMS, PMS and MPP sputtered CrN coatings as a function of the average target power for a given working pressure of 5 mTorr, an Ar/N₂ flow ratio of 1:1 and a substrate target distance of 140 mm. An almost linear increase in the deposition rate as the average target power was increased is evident for all three techniques. For a given average target power, the dcMS exhibited the highest deposition rate, the MPP deposition exhibited a slightly lower deposition rate than that of the dcMS, while the PMS exhibited the lowest deposition rate. It was also observed that the difference in the deposition rate between the PMS deposition and other two sputtering techniques increased with the increase in the average target power. In the bipolar PMS pulse, since the positive sputtering ions will be repelled away from the target by the positive cathode voltage during the reversed pulse period, the higher positive voltage applied on the target probably changes the sputter yield of the target at a higher target power.

The different characteristics of dcMS, PMS and MPP plasmas significantly affected the structure and properties of the deposited CrN coatings. Fig. 5 shows the XRD patterns of dcMS, PMS and MPP sputtered CrN coatings deposited at a floating substrate bias voltage. All coatings exhibit a NaCl type face center cubic (fcc) structure with (111), (200) and (220) reflections. The Cr peak at 44.5° in all diffraction patterns is from the Cr adhesion layer. The diffraction peaks of the PMS CrN coating shifted to lower angles as compared to the coatings deposited by dcMS and MPP. Residual stress measurements indicated that the PMS CrN coating exhibited a higher compressive residual stress of −2.0 GPa than that of the dcMS and MPP CrN coatings (Table 2). Since all CrN coatings have a similar N:Cr ratio in a range of 0.94–0.98, the shift of the diffraction peaks in the PMS CrN coating is due to its higher compressive residual stress, which was possibly generated by the ion bombardment from the high energy ions (> 30 eV) in the PMS plasma (Fig. 3). The average grain size of the coatings was estimated by the Scherrer formula using the (200) reflection [30]. The average grain size of the dcMS CrN coating was 105 nm. The grain size of the PMS CrN coating decreased to 78 nm. A further decrease in the grain size to 45 nm was found in the MPP-1 CrN coating, which was deposited at a same average target power of 1 kW. However, the grain size of the MPP-2 CrN coating increased to 60 nm as the average target power was increased to 4 kW, which is probably related to a higher deposition rate and a higher thermal energy on the substrate.

Fig. 6 shows the cross-sectional and top view SEM micrographs of four CrN coatings deposited at a floating substrate bias, and Fig. 7 shows the cross-sectional TEM micrographs of the dcMS, PMS and MPP-2 CrN coatings.

The dcMS CrN coating exhibited large columnar grains and porous structure throughout the coating thickness (Fig. 6a). The tops of the grains exhibited a plate like shape as seen in the SEM view (Fig. 6b). The size of the tops of the grains was as large as 200–250 nm. TEM study confirmed that the dcMS CrN coating consists of large columnar grains (100–150 nm) with a large amount of porous regions (Fig. 7a). The surface roughness of the dcMS CrN coating was 27.5 nm as measured using the optical profilometer.

The PMS CrN coating also consists of long columnar grains which extend over the coating thickness. However, the width of the grains considerably decreased as compared to that of the dcMS CrN coating, as shown in Fig. 6c. The size of the top of the plate shaped grains reduced to 100–150 nm (Fig. 6d). The TEM micrograph shown in Fig. 7b revealed a columnar structure with the columnar grain size in the range of 50–80 nm. Nevertheless, the boundaries/voids between
the columnar grains were still clearly identified. The selected area diffraction pattern (SAED) confirmed a polycrystalline fcc CrN structure and that the grain size of the coating is in the nanometer scale. The surface roughness of the PMS CrN coating decreased to 17.4 nm.

Fig. 6e and f shows the SEM micrographs of the MPP-1 CrN coating. Fig. 6g and h shows the SEM micrographs of the MPP-2 CrN coating. It is evident that both MPP sputtered coatings exhibited a denser microstructure and finer grain size as compared to the dcMS and PMS coatings. The interruption of the large columnar grain growth accompanied with the development of short grains was revealed in Fig. 6e and g. The shape of the tops of the grains changed to random equiaxed shape, and the size of the tops of the grains further decreased to be less than 100 nm (Fig. 6f and h). In addition, low surface roughness values of 5.7 and 8.2 nm were measured in the MPP-1 and MPP-2 CrN coatings, respectively. The TEM micrograph of the MPP-2 CrN coating revealed a fully dense microstructure without clear grain boundaries, as shown in Fig. 7c. The width of the short columnar grains estimated from the TEM observation is less than 50 nm.

3.3. Mechanical and tribological properties of CrN coatings

The mechanical and tribological properties of dcMS, PMS and MPP sputtered CrN coatings are summarized in Table 2. The H/E ratio (resistance against elastic strain to failure) was evaluated as an important and valuable parameter for tribological coating performance. A higher H/E ratio of coatings is expected to allow the redistribution of the applied load over a large area, delaying failure of the film [34]. The dcMS CrN coating showed a low hardness of 16 GPa and a Young’s modulus of 280 GPa, which result in a low H/E ratio of 0.057. The hardness value and H/E ratio were increased to 21 GPa and 0.082 respectively in the PMS CrN coating. On the other hand, high hardness values of 24.5 and 26 GPa and H/E ratio of 0.086 and 0.084 were found in the MPP-1 and MPP-2 CrN coatings, respectively. The improved hardness and H/E ratio in the MPP CrN coatings as compared to the dcMS and PMS CrN coatings can be attributed to its denser microstructure and the grain boundary hardening by Hall–Petch relationship with a decreased grain size due to the high ion flux bombardment on the growing films from the MPP plasma.

The adhesion of the coatings was evaluated using the microscratch test. The scratch track images were presented in Fig. 8, which also shows the critical coating failure events as suggested by Stallard et al. [35]. Since the thin Cr adhesion layer was deposited using the same power source (dcMS, PMS and MPP) as the top CrN coating, the overall Cr/CrN coatings exhibited different adhesion behaviors.

As shown in Fig. 8a for the dcMS CrN coating, there is a combined LC1 (the critical load for the first cracking) and LC2 (the critical load for the first adhesive chipping at the edge) at 12 N. The LC3 (the critical load for the first coating delamination within the track) was found at 20 N. There is no LC4 (the critical load for the massive coating delamination) identified at the end of the scratch test.

The PMS CrN coating exhibited deceased adhesion strength as compared to the dcMS CrN coating. The LC1 and LC2 occurred at the same load of 9 N as shown in Fig. 8b. It also shows low LC3 and LC4 critical loads at 15 and 23 N, respectively. The continuous spallation of the PMS CrN coating at the edge and within the scratch track indicates a poor adhesion of the coating.

The MPP-1 CrN coating showed improved adhesion strength as compared to the dcMS and PMS CrN coatings. The LC1 and LC2 occurred at the same load of 9 N as shown in Fig. 8c. However, there is no coating delamination within the track until the load was increased to 28 N. The MPP-2 CrN coating exhibited further improved adhesion strength. As shown in Fig. 8d, the coating exhibited a smooth scratch track with an LC2 = 16.2 N and an LC3 = 28 N. There is no LC4 observed at the end of the scratch track for both MPP sputtered CrN coatings. It should be noted that the relatively low critical loads for all coatings are related to the soft stainless steel substrate used in the current study. Similar microscratch tests were performed on the coatings deposited on a hard tool steel substrate. No coating failure was observed for all coatings at a maximum load of 30 N. A typical example of the scratch...
and decreased wear rates of 2.43 and 2.4×10^{-1} are shown in Fig. 9. Two dimensional (2D) cross-sectional profiles of the wear tracks were summarized in Table 2. Three dimensional (3D) morphologies of the WC-Co ball were measured using the ball-on-disk test and the results show a rough surface (Fig. 6b) and a low hardness (16 GPa). The 2D wear track profile shows a wear depth of 1750 nm and the 3D morphology confirms a large amount of wear debris along the sides of the wear track (Fig. 9). A decrease in the COF value (0.45) and wear rate (3.65×10^{-6} mm^3 N^{-1} m^{-1}) was observed for the PMS CrN coating due to a decrease in the surface roughness and an increase in the coating hardness. The wear depth was decreased to 900 nm for the PMS CrN coating (Fig. 9).

MPP-1 CrN and MPP-2 CrN coatings exhibited low COF of 0.36 and 0.33 and decreased wear rates of 2.43 and 2.4×10^{-6} mm^3 N^{-1} m^{-1}, respectively (Table 2). As shown in Fig. 9, the wear track of the MPP-2 CrN coating is shallow and smooth without extensive debris. The wear depth was further decreased to 600 nm.

4. Discussion

The above results have demonstrated that there is a strong correlation between the plasma properties generated in different sputtering techniques and the resultant microstructure and properties of the deposited CrN coatings. Since the substrate bias was maintained at a constant value of 250 A, the ion energy, the number of ions and the substrate potential for all depositions, the ion bombardment on the growing film largely depended on the intrinsic plasma properties, including the ion energy, the number of ions and the substrate floating potential.

In the dcMS plasma, the ion energy and the number of ions are low. Additionally, the majority of the ions is from the gas species (Ar^+ and N_2^+), while the number of the metal ions (Cr^+) from the target material is rare (Fig. 3d). The small ion to neutral ratio (ion flux) and the low ion energy in the dcMS plasma are not able to provide sufficient ion bombardment on the growing film. Therefore, the mobility of the adatoms on the substrate is too low to allow them to diffuse due to the low kinetic energy delivered to the adatoms. This condition will lead to the development of a porous microstructure containing large columnar grains with a rough surface (Figs. 6 and 7). Consequently, the dcMS CrN coating exhibited a low hardness, low adhesion and wear resistance as demonstrated in the nanoindentation, microscratch and ball-on-disk wear tests.

In the PMS plasma, the total numbers of gas and metal ions increased as compared to those of the dcMS plasma (Fig. 3d). In addition, a large portion of the ions was generated by the high ion energy peak at 30–50 eV in the current pulsing condition (Fig. 3). The increased ion flux with higher kinetic energy in the PMS plasma provided increased ion bombardment on the growing film, which led to a reduction in the grain size, a decrease in the surface roughness and an increase in the density as compared to the dcMS CrN coating (Figs. 6 and 7). The improved coating microstructure led to an increase in the coating hardness and wear resistance. However, it is also noted that the PMS CrN coating still did not achieve a fully dense structure without the aid of the substrate bias. The PMS CrN coating showed a poor adhesion on the soft stainless steel substrate in the microscratch test (Fig. 8), which is possibly related to its lower coating thickness due to its lower deposition rate and higher residual stress generated by the higher ion energy bombardment.

As suggested by Petrov et al. [1], it is possible to deposit fully dense films with a low residual stress when there is a higher ion to neutral ratio but with a low ion energy (<20 eV). As shown in Fig. 3d, the MPP plasma exhibited a significant increase in the numbers of both target material (Cr^+) and gas (Ar^+ and N_2^+) ions as compared to the dcMS and PMS...
Fig. 9. Three dimensional micrograph and two dimensional profile of the wear tracks of dcMS, PMS and MPP-2 CrN coatings after sliding against a WC-Co ball at a normal load of 3 N for a sliding distance of 150 m.
throughout the coating thickness, as evident in Fig. 6e and g. It should be noted that similar behaviors of the coating microstructure improve-ments have also been observed for CrN films grown by HPPMS.[27–29]. The hardness of the MPP CrN coatings deposited with a floating substrate bias using the dcMS and PMS techniques as reported in various references [24–26]. Since the residual stress levels in the MPP CrN coatings are relatively low (Table 2), it is believed that the improved hardness and wear resistance in the MPP CrN coatings are mainly due to the improved coating density, decreased grain size and smooth surface roughness resulting from the enhanced low energy ion bombardment from the intense MPP plasma. This result demonstrated that it is possible to produce high quality CrN coatings without the need of the substrate bias to achieve a low residual stress and defects incorporation, which is critical for producing thick tribological coatings with a good adhesion.

5. Conclusions

CrN coatings were deposited in a closed field unbalanced magnetron sputtering system at a floating substrate bias using the dcMS, PMS and MPP techniques. The plasma diagnostics demonstrated a small number of ions with low ion energy in the dcMS plasma. An increase in the number of ions together with the generation of multiple high ion energy regions was revealed in the PMS plasma. The MPP plasma exhibited a low peak ion energy at 4 eV, whereas the number of ions (especially for the target metal ions) was significantly higher than in the dcMS and PMS plasmas. It was found that the deposition rate of the MPP CrN coatings was slightly lower than those of the dcMS depositions, but higher than in the PMS depositions at similar average target powers. The CrN coatings deposited by the high density and ionization degree MPP plasma with a floating substrate bias exhibited a denser microstructure showing the interruption of the columnar grain growth, a finer grain size and a smoother surface as compared to those of the dcMS and PMS CrN coatings. The improved microstructure in the MPP CrN coatings led to high hardness (24.5 and 26 GPa), excellent wear resistance (COF = 0.33 and 0.36) and improved adhesion.

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References