Microstructure and mechanical properties of CrN films fabricated by high power pulsed magnetron discharge plasma immersion ion implantation and deposition

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Abstract

CrN films with strong adhesion with the substrate have been fabricated on Ti6Al4V alloy using novel plasma immersion ion implantation and deposition (PIII&D) based on high power pulsed magnetron sputtering (HPPMS). A macro-particle free chromium plasma is generated by HPPMS while the samples are subjected to high voltage pulses to conduct PIII&D. The CrN coatings have a dense columnar structure and low surface roughness. The grains in the films have the face-centered cubic (fcc) structure with the (200) preferred orientation. An excellent adhesion is achieved with a critical load up to 74.7 N. An implantation voltage of 18 kV yields a hardness of 18 GPa and better wear resistance and a low friction coefficient of 0.48 are achieved.

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1. Introduction

Since its inception in the 1980s, plasma-based ion implantation (PBI) or plasma immersion ion implantation and deposition (PIII&D) have been applied successfully to surface modification and thin film deposition [1,2]. In contrast to conventional beam-line ion implantation, the sample is surrounded by the plasma and subjected to negative high voltage pulses. In this way, energetic ion bombardment introduces ion mixing effects that enhance film adhesion and an abrupt interface between the film and substrate can be avoided [3], and the line-of-sight restriction of beam-line ion implantation is also circumvented. However, when metal ions are implanted using the pulsed cathodic arc technique, droplets called macro-particles are inevitably produced due to the energetic process on the cathode surface [4,5]. Macro-particles degrade the performance of the films and are normally not acceptable in most applications. A common method to eliminate macro-particles from the drifting plasma is to use a curved magnetic filter [6–8], but it may decrease the plasma flux and consequently the process efficiency. In 1999, high power pulsed magnetron sputtering (HPPMS) was proposed by Kouznetsov et al. to produce high density metal ions without droplets [9–11]. We have introduced the hybrid HPPMS–PIII&D technique [12,13] which combines the advantages of PIII&D and HPPMS, and there are no macro-particles in the high density metal plasma. Additionally, since the target used to produce the plasma is a common magnetron sputtering target, it is easy to scale up for large and industrial components.

In HPPMS–PIII&D, the high-voltage pulse has a critical effect on the structure and properties of the prepared coatings. In this work, the surface morphology, microstructure, and surface properties of CrN coatings fabricated on silicon and Ti6Al4V alloy are investigated and the effects of the high voltage are evaluated.

2. Experimental details

The experiments were performed in turbo-molecular pumped high-vacuum chamber with a diameter of 40 cm and height of 40 cm (Fig. 1). The chamber was evacuated to a base pressure of $3 \times 10^{-3}$ Pa. The carrier gas (Ar, 99.9997% pure) and reactive gas (N$_2$, 99.998% pure) were introduced through a leak valve. A Cr target (50 mm in diameter, 6 mm thick, and 99.9% pure) was mounted on an unbalanced magnetron cathode. The magnetron cathode was driven by a hybrid pulsed power supply developed in our laboratory [14]. The power supply was able to deliver either DC with a power of
5 kW or pulses with a peak power of 216 kW (1200 V and 180 A) at a repetition frequency of 20–200 Hz and pulse width ranging from 20 μs to 400 μs. The substrate was biased by a pulsed power supply delivering pulses with a maximum voltage of 30 kV, repetition frequency of 20–200 Hz, and pulse width of 20–500 μs.

Silicon (1 0 0) and Ti6Al4V alloy samples (20 mm in diameter and 3 mm thick) were used as substrates. The Ti6Al4V samples were polished to a mirror finish using 1 μm diamond paste. Prior to loading into the chamber, the substrates were ultrasonically cleaned in ethanol and acetone for 20 min. The substrates were placed at a distance of 16 cm from the target and no external heating was applied during the process. The experiments were carried out in four stages. Firstly, plasma etching was performed using a high-voltage self-excited glow discharge in argon. Secondly, a Cr layer was deposited on the Ti6Al4V and Si (1 0 0) substrates by HPPMS–Pill&D in argon to increase the adhesion between the film and substrate. Thirdly, the CrN film was deposited by reactive HPPMS–Pill&D using the two gases under different high voltage biases. Finally, the samples were cooled naturally in vacuum. The important processing parameters are listed in Table 1.

The microstructure of the films was examined by scanning electron microscopy (SEM) on the Hitachi S4800. The nano-scale surface morphology and roughness were characterized by atomic force microscopy (AFM). The phase composition of the films was determined by X-ray diffraction (XRD) in the Bragg-Brentano geometry. To assess film adhesion, the critical loads, $L_c$, were measured on the MFT-4000 scratch tester with a diamond tip with a radius of 200 μm, maximum load of 100 N and scratch length of 4 mm. The hardness and Young’s modulus of the coatings were measured by an MTS nano-indenter XPII equipped with a Berkovich diamond indenter with the depth of 400 nm. The wear resistance of the samples was evaluated by a home-made ball-on-disc tester under ambient conditions (relative humidity of 25 ± 1 % and temperature of 20 ± 1 °C) by sliding against a Φ6 mm GCr15 ball with the load of 100 g at a speed of 50 r/min and a wear radius of 2 mm.

### Table 1

<table>
<thead>
<tr>
<th>Step</th>
<th>Process</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Plasma etching</td>
<td>Ultimate vacuum = 1.0 × 10⁻³ Pa, high voltage pulse = −10 kV, frequency = 50 Hz, width = 200 μs, Ar flow rate = 10 sccm, working pressure = 0.1 Pa, 15 min</td>
</tr>
<tr>
<td>2</td>
<td>Cr interlayer</td>
<td>High voltage pulse = −10, −14, −18, −22 kV, frequency = 50 Hz, width = 50 μs, Phase = −150 μs, HPPMS pulse = 900 V, frequency = 50 Hz, width = 200 μs, DC = 0.2 A, Ar flow rate = 10 sccm, working pressure = 0.5 Pa, 5 min</td>
</tr>
<tr>
<td>3</td>
<td>CrN film</td>
<td>High voltage pulse = −10, −14, −18, −22 kV, frequency = 50 Hz, width = 50 μs, HPPMS pulse = 900 V, frequency = 50 Hz, width = 200 μs, DC = 0.2 A, Ar flow rate = 10 sccm, N₂ flow rate = 6 sccm, working pressure = 0.5 Pa, 60 min</td>
</tr>
<tr>
<td>4</td>
<td>Cooling down</td>
<td>Vacuum pressure = 1.0 × 10⁻³ Pa, 30 min</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Samples</th>
<th>10 kV</th>
<th>14 kV</th>
<th>18 kV</th>
<th>22 kV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface roughness, $R_a$ (nm)</td>
<td>5.778</td>
<td>7.410</td>
<td>7.139</td>
<td>21.226</td>
</tr>
<tr>
<td>Mean size surface roughness (nm)</td>
<td>219.42</td>
<td>220.36</td>
<td>240.12</td>
<td>395.26</td>
</tr>
</tbody>
</table>

3. Results and discussion

In contrast to the Pill&D based on the pulsed cathodic arc technique,[15,16] HPPMS–Pill&D can produce a high density plasma without metal droplets [13]. Consequently, highly efficient deposition and better film quality can be achieved. The AFM images obtained from the CrN films (4 μm × 4 μm) deposited on silicon wafers at high-voltage of −10 kV, −14 kV, −18 kV, and −22 kV are shown in Fig. 2(a)–(d), respectively. The films deposited at lower voltages (e.g., −10 kV and −14 kV) show small granular microstructures which stem from radiation damage by high energy ion bombardment [17].

Table 2 shows the surface roughness and mean size of the surface roughness on CrN films deposited on Si. The surface roughness increases with bias voltage. The gradual transition in the film surface from a small granular structure to larger sized surface can be attributed to enhanced thermal diffusion and adatom mobility as the energy of the incident ions increases [18].

Fig. 3 depicts the cross-sectional SEM micrographs of the CrN coating deposited on Si at −18 kV. Granular grains form near the interface between substrate and substrate. With the film depositing, the micrography evolves into densely packed structure. But this is evidently different from columnar structure obtained in conventional DC magnetron sputtering [19]. The top section of the films seems to grow on the discontinuous columns due to re-nucleation. The structure near the surface is not clearly identifiable, with many column boundaries being obscured. This indicates that adatoms have a high mobility and might be able to diffuse between columns.

A similar dense columnar structure is achieved by A.P. Ehi-asarian [20], and the high mobility of the adatoms induced by bombardment with highly energetic ions is considered to fill surface vacancies and crevices combined with dynamical etching of protruding features. A transition from polycrystalline to nanocrystalline or amorphous films is found by Alami [21] and Broitman [22] with the increase of target current. Greczynski et al. [19,23] have deposited CrN films with different N contents using HPPMS and found the samples with lower and higher nitrogen content were characterized by a dense columnar structure and the columnar growth was suppressed by the β-Cr₂N phase. In our investigation, the CrN phase is dominated in the films (shown below), and the films exhibit a densely packed columnar microstructure.
Fig. 2. Typical three-dimensional AFM images of CrN films deposited on Si (1 0 0) substrate at (a) −10 kV, (b) −14 kV, (c) −18 kV, and (d) −22 kV.

Fig. 4 shows the thickness of the CrN films fabricated on Si at different voltages. The bias voltage has an obvious effect on the deposition rate. The film thickness increases with bias voltage from −10 to −22 kV. The estimated deposition rates at bias voltage of −10, −14, −18, and −22 kV are 17.7, 20.8, 23.3, and 24.8 nm/min, respectively. Compared to 15.5 nm/min deposition rate with DC bias of −100 V, a higher deposition rate is achieved with a higher sample bias during HPPMS–PIII&D processes.

HPPMS has been reported to suppress the deposition rate compared to conventional DC processes at the same average power [10,22], particularly for materials with low sputtering yields. A pathway model has been proposed by Christie to explain the results that when the sputtered metal particles are ionized, some of ions can be captured and directed to the target due to the low potential on the samples. Hence, these metal ions which fly to the target are not available for deposition on the substrate [24,25]. In this work, however, the spatial electric field is changed due to the high voltage applied to the substrate and consequently, more ions are attracted and fly to the substrate from all directions and this will surely lead to a high deposition rate during the HPPMS–PIII&D processes compared with conventional HPPMS with no bias or low

Fig. 3. Cross-sectional micrographs of CrN films deposited on Si (1 0 0) substrate at −18 kV.

Fig. 4. Thickness of CrN films deposited on Si (1 0 0) substrates at different biased voltages.
bias. It is noteworthy that a higher deposition rate has been recently achieved using MPP method [26,27].

Fig. 5 shows the crystalline microstructure of the films deposited on the Ti6Al4V substrate at different bias voltages. All the films are highly textured with the (2 0 0) preferential orientation with the corresponding 2θ of −43.3°, but the intensity of other orientations is quite low. Generally, polycrystalline films are expected to have multiple orientations to minimize the total energy [28]. For the fcc CrN films, the (2 0 0) preferential orientation indicates very low intrinsic stress that may be released by atomic mobility and thermal diffusion induced by ion bombardment [29]. The relative intensity of the preferential orientation in the CrN (2 0 0) direction increases with voltage from −10 to −18 kV. However, the peak intensity of CrN (2 0 0) may decrease if the voltage further increases. The difference is indicative of the variation in the number of oriented grains [30].

The adhesion between the CrN films and Ti6Al4V substrate is evaluated by scratch tests. Fig. 6 shows the scratch track and the critical loads of the films and substrates. With increasing of loads, the width and thickness of the scratch track increase progressively. Until the critical loads (Lc), the first delamination appears, and consequently mass delamination happens. All the coatings demonstrate excellent adhesion as indicated in Fig. 6. With the sample bias increasing, the critical load Lc increases gradually and a maximum of 74.7 N is achieved at −22 kV.

A higher critical load of 85 N has been obtained by Ehiasarian et al. [31,32] from CrN films deposited on HSS substrate by HPPMS. In his work, the HSS substrate is bombarded by high energy metal ions (1200 eV) from the HPPMS discharge for 30 min before CrN film deposition. Substantial ion implantation effect and local

**Fig. 5.** XRD spectra of CrN films deposited on Ti6Al4V substrates at different high voltages.

**Fig. 6.** Images of scratch tracks between the CrN films and Ti6Al4V substrate deposited at different high voltages.

**Fig. 7.** Hardness and Young’s modulus of CrN films deposited on Ti6Al4V.

**Fig. 8.** Friction coefficients of the samples deposited at different high voltages.

**Fig. 9.** Width and depth of wear tracks deposited at different high voltages.
epitaxial growth are observed in conjunction with efficient cleaning of the substrate. In addition, the substrate is also heated to 250 °C to increase the mobility of the incident atoms. In our experiments, only 10 min of plasma etching pre-treatment is implemented without extra heating. Many films prepared by PBIID have a gradient layer in the near surface due to intense bombardment of highly energetic ions that will reduce the stress between different materials on the two sides of the interface and improves the adhesions [33–35]. As a new PBIID technique, a gradient layer is surely formed by ion bombardment and implantation in HPPMS–PIID, which induces the high critical load \( L_c = 74.7 \text{ N} \).

In addition to the excellent adhesion, high nano-hardness and Young’s modulus are obtained, as shown in Fig. 7. The hardness and Young’s modulus increase significantly from 4.6 GPa and 120.2 GPa of the Ti6Al4V substrate to 18 GPa and 211 GPa of the CrN film deposited at −22 kV, respectively. The hardness is a little lower than that (20–24 GPa) reported in the literature [31,36]. This may be attributed to the larger amount of heat carried by highly energetic ion bombardment.

As the voltage increases, the hardness goes up gradually. It is well known that high voltage pulses can induce the formation of dense structures and supersaturated solid solutions in films to enhance the hardness [37].

Fig. 8 shows the friction coefficient measured from different samples fabricated on Ti6Al4V versus sliding time in the pin-on-disk tests. All the CrN films show lower friction coefficient (0.45–0.5) than the untreated substrate (0.65). Fig. 9 displays the depth and the width of the wear track after the test. The wear track width becomes narrow and the depth becomes smaller as the voltage increases. Both features indicate the better tribological properties.

4. Conclusion

CrN films are fabricated on silicon and Ti6Al4V by HPPMS–PIID. The films have a well defined densely packed columnar structure with low surface roughness. The coatings have the fcc structure with the preferred CrN (2 0 0) orientation. The XRD peak intensity increases with increasing negative voltages up to −18 kV. The critical load determined by scratch tests reaches 74.7 N. The high voltage also improves the mechanical properties.

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