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Influence of Nitrogen Partial Pressure and Substrate Bias on the Mechanical Properties of VN Coatings

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Abstract

Vanadium nitride coatings were deposited via magnetron reactive sputtering system with varying nitrogen partial pressures and negative substrate bias to further understand the influence of the sputtering conditions on the microstructure and the mechanical performance. Grazing incidence X-ray diffraction, field emission scanning electron microscopy equipped with energy dispersive X-ray and X-ray photoelectron spectroscopy were used to characterize the microstructure; nano-hardness tester and profilometer were used to measure the mechanical performance. By varying the nitrogen partial pressures from 0.007 Pa to 0.29 Pa, more compact coating with higher hardness (22.9 GPa) was achieved at 0.29 Pa. In parallel, the influence of bias voltage on the residual stress and hardness was significant.

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Keywords: VN; coating; microstructure; mechanical performance

1. Introduction

High speed and dry cutting poses tougher challenges to the protective coatings, such as low-friction and lubricating in addition to mechanical properties [1]. Intrinsic solid lubricants like DLC, MoS2, and h-BN often begin to fail their tribological effectiveness at elevated temperatures, in humid atmosphere or due to oxidation. The same happen to other lubricants from chemical reactions between coating and moisture of the ambient atmosphere. In recent years, Magnéli-phase, which is one kind of high-
temperature lubricious oxide materials with easy moveable shear planes, has attracted increasing interests. [2, 3] These phases exhibit good thermal stability and tribological property [3, 4]. Among these materials, vanadium easily oxidizes at high temperature and its melt forms a lubricant layer [3]. Consequently, a lot of efforts have been made to develop vanadium nitride hard coating, such as TiN/VN, TiAlN/VN, and CrAlVN coatings, to combine high hardness and high temperature lubricant properties into one [1]. Compared with TiN and CrN, studies on the vanadium nitride coatings limited are far behind [5, 6, 7].

In this study, VN coatings were prepared via magnetron reactive sputtering. The influence of nitrogen partial pressure ($P_{N_2}$) and negative substrate bias voltage ($V_b$) on the microstructure, and mechanical performance were investigated.

2. Experimental

2.1. Sample preparation

VN coatings were deposited by reactive magnetron sputtering (JGP 560C4, CAS SKY Technology Development Co., Ltd., China). Hot-pressed vanadium target (99.95 at.% in purity, 70 mm in diameter, and 5 mm in thickness) was used. The substrate was silicon wafer (100). The distance between the target and substrate was kept in 60 mm. Before loading, the substrates were ultrasonically cleaned in acetone, ethanol and deionized water in sequence for 15 min, followed by rapid drying with nitrogen blow. Before deposition, the target surface was pre-sputtered in pure argon (Ar) plasma for 10 min.

Two series of VN coatings were fabricated, one in varying nitrogen partial pressure and the other in varying substrate bias (Table 1).

Table 1 Sputtering parameters of VN thin coatings.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target/diameter</td>
<td>V(99.95 at%) /70 mm diameter</td>
</tr>
<tr>
<td>Substrate</td>
<td>(100) Si single crystal wafer</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Distance between target and substrate (mm)</td>
<td>60</td>
</tr>
<tr>
<td>Base pressure (Pa)</td>
<td>$4.4 \times 10^{-4}$</td>
</tr>
<tr>
<td>Working pressure (Pa)</td>
<td>0.35</td>
</tr>
<tr>
<td>Target power density (W/cm$^2$)</td>
<td>~1</td>
</tr>
<tr>
<td>Deposition time (h)</td>
<td>2.5</td>
</tr>
<tr>
<td>$N_2$ partial pressure (Pa)</td>
<td>0.007, 0.01, 0.03, 0.6, 0.12, 0.18, 0.23, 0.29</td>
</tr>
<tr>
<td>Bias voltage (--V)</td>
<td>0, 50, 100, 150, 200</td>
</tr>
</tbody>
</table>

2.2. Characterization

The crystalline structure was characterized by grazing incidence X-ray diffraction (GIXRD). A D/max2550HB+/PC X-ray diffractometer with Cu Kα radiation (15 kV and 10 mA) at a scan rate of 2°/min was employed. The scanning angle was performed from 30° to 90° at a step size of 0.02° and the incident angle was set at 1°. Texture coefficients (TC) of (111), (200), (220) and (311) reflections were determined from the intensities of VN peaks [8]. Assuming no significant micro-strain, the average grain size was estimated by the Debye-Scherrer formula [9].

The coating thickness, surface and cross-sectional morphology were studied by field emission scanning electron microscopy (SEM, BCPCAS 4800). Energy dispersive X-ray (EDX) attached to the
SEM was adopted to analyze the chemical compositions. X-ray photoelectron spectroscopy (XPS, PHI 5300) was also applied to confirm the element concentration. The residual stress $\sigma$ was obtained from the change in the radius of curvature of the Si substrate before and after deposition, using Taylor-Hobson (SP-120) profilometer and Stoney’s equation [10]. The hardness of the coatings was determined by nanoindentation (CSEM-NHT) with a Berkovich diamond tip. The indent depth was 70 nm (less than one tenth of the coating thickness to minimize the substrate effect) at a loading speed of 4 nN/min and maximum load of 2 mN.

3. Results and discussion

3.1. Effect of $N_2$ partial pressure ($P_{N_2}$)

With $N_2$ partial pressure ($P_{N_2}$) increasing from 0.007 Pa to 0.29 Pa, the deposition rate of the coatings dropped from 9.5 nm/min to 6.5 nm/min, as shown in Fig. 1. Two reasons are identified: the poor sputtering yield with $N_2$ compared with Ar; [11] and “target poison” [7, 12]. The N/V atomic ratio of VN coatings with $P_{N_2}$ increasing is plotted in Fig. 2; the ratio increased from 0.58 to 1.09 (EDX, Fig. 2a) due to the increasing concentration of reactive nitrogen ion in the chamber. XPS results confirmed this trend ($P_{N_2}=0.01$ Pa, N/V=0.68; $P_{N_2}=0.18$ Pa, N/V=0.89; $P_{N_2}=0.29$ Pa, N/V=1.09), as shown in Fig. 2b.

![Fig. 1 Deposition rate of VN coatings at different $P_{N_2}$.](image)

![Fig. 2 N/V atomic ratio of VN coatings at different $P_{N_2}$; a. EDX, b. XPS.](image)
Figure 3 shows the XRD spectra of VN coatings deposited at different PN2. Only a single phase of fcc-VN with reflections corresponding to (111), (200), (220) and (311) planes are observed. The changes in the preferred orientation as a function of PN2 are qualitatively estimated in terms of texture coefficients (TC), as shown in Fig. 4. With PN2 increased, the coatings show a preferential orientation of (111) plane. In the meanwhile, the grain size decreased from 12.9 nm to 9 nm as PN2 increased (Fig. 5).

Figure 6 shows the SEM surface morphology and cross section images of VN coatings deposited at different PN2. (a, b) PN2 =0.03 Pa, Vb=0V, (c, d) PN2 =0.18 Pa, Vb=0V.
The surface and cross-sectional morphology of VN coatings (P_{N2}=0.03 and 0.18 Pa) were shown in Fig. 6. At 0.03 Pa (P_{N2}), the surface morphology shows a multi-faced structure and rather rough appearance, while cross-sectional observation also expressed the loose structure. At 0.18 Pa (P_{N2}), the structure of the coating became compact.

Figure 7 shows the residual stress of VN coatings. When P_{N2} was lower than 0.03 Pa, the residual stress was very low, and can be neglected due to the loose structure of the VN coatings. With increase of P_{N2}, a slowly increasing of compressive stress was observed up to ~0.4 GPa, as the structure became denser, and the stress induced by sputtering could not be released thus compressive stress increased. Figure 8 shows hardness of VN coatings. The hardness increased from 9 GPa to 23.3 GPa when the P_{N2} increases from 0.007 Pa to 0.23 Pa, as the crystallite size became smaller, in good agreement with Hall-Petch law [13].

3.2. Effect of substrate bias voltage (V_b)

With substrate bias voltage (V_b) changed from 0 V to ~200 V, the deposition rate of the coatings dropped from 6.7nm/min to 5.6nm/min, as shown in Fig. 9. As negative V_b is applied to the substrate,
positive ions of the plasma are attracted toward the substrate and transfer their kinetic energy to the surface atoms. As the $V_b$ increases, the incident ion energy increases, and as a result, re-sputtering from the deposited surface may take place, resulting in decreased deposition rate [14, 15]. The influence of $V_b$ on the N/V atomic ratio was shown in Fig. 10, similar with the results of [15]. In this process, the N/V atomic ratio increased from 0.85 to 0.98 (EDX, Fig. 10a) as revealed by XPS results ($V_b=0$ V, N/V=0.89; $V_b=-200$ V, N/V=1.02) shown in Fig. 10b. The increase is attributed to the increase of ionized N atoms [16].

Figure 11 is the XRD spectra of VN coatings deposited at different $V_b$. The coatings grown without bias have a preferred orientation of (111) plane; and under weak ion-irradiation conditions at –50V, –100V and –150V contain predominantly a mixture of (111) and (200) orientations with a small volume fraction of (220) orientation. The coatings deposited at high bias voltage of –200 V have a dominant (111) texture. The changes in the preferred orientation as a function of the bias voltage are qualitatively further estimated in terms of coefficients ($T_C$) of texture as shown in Fig. 12. Meanwhile the crystallite size tends to decrease from 0V to –150 V, and then increases as the substrate bias voltage ranges from –150 V to –200 V, as shown in Fig. 13. As more defects will be generated on the surface of growing coating with the increase of incident ion energy the nucleation sites will increase [17], as a result the crystallite sizes of

![Fig. 10 N/V atomic ratio of VN coatings at different Vb; a. EDX, b. XPS.](image)

![Fig. 11 XRD spectra of VN coatings deposited at different Vb with P$_{N_2}$=0.18 Pa.](image)
the coatings decrease. Further increasing the substrate bias voltage to −200 V, because of high energy ions bombardment on the coatings will induce higher temperature which would promote crystallite size.

The surface morphology and cross section images of VN coatings deposited at −150 V and −200 V were shown in Fig. 14. At \( V_b \) of −150 V, the crystal structure is equiaxial; at −200 V, the structure became columnar, with smoother surface as a result of re-sputtering.

![Fig. 12 Texture coefficient of VN coatings deposited at different \( V_b \).](image1)

![Fig. 13 Crystallite size of VN coatings deposited at different \( V_b \).](image2)

Fig. 12 Texture coefficient of VN coatings deposited at different \( V_b \).

Fig. 13 Crystallite size of VN coatings deposited at different \( V_b \).

![Fig. 14 SEM surface morphology and cross section images of VN coatings; (a, b) \( P_{N_2} = 0.18 \) Pa, \( V_b = -150 \) V, (c, d) \( P_{N_2} = 0.18 \) Pa, \( V_b = -200 \) V.](image3)

![Fig. 14 SEM surface morphology and cross section images of VN coatings; (a, b) \( P_{N_2} = 0.18 \) Pa, \( V_b = -150 \) V, (c, d) \( P_{N_2} = 0.18 \) Pa, \( V_b = -200 \) V.](image4)

Fig. 14 SEM surface morphology and cross section images of VN coatings; (a, b) \( P_{N_2} = 0.18 \) Pa, \( V_b = -150 \) V, (c, d) \( P_{N_2} = 0.18 \) Pa, \( V_b = -200 \) V.

The surface morphology and cross section images of VN coatings deposited at −150 V and −200 V were shown in Fig. 14. At \( V_b \) of −150 V, the crystal structure is equiaxial; at −200 V, the structure became columnar, with smoother surface as a result of re-sputtering.
Figure 15 shows the residual stress of VN coatings with varying $V_b$. When $V_b$ increased from 0 V to –150 V, there is a rapidly increase of compressive stress from –0.36 GPa to –1.69 GPa due to increased bombardment of incident ions; but from –150 V to –200 V, the residual stress slowly reduced to –1.62 GPa, suggesting temperature’s annealing effect at energetic bombardment. Fig. 16 plots hardness of the VN coatings at different substrate bias voltage. The increase of hardness from 20.4 GPa to 24.5 GPa with the bias from 0V to –200 V is due partly to the increased compressive stress and partly to the denser structure.

4. Conclusions

In reactive magnetron sputtering of VN coatings, increasing of the nitrogen partial pressure (from 0.007 Pa to 0.29 Pa) brings about denser coatings with higher hardness (22.9 GPa). Increasing of substrate bias voltage generates more residual stress in the coating (–1.62 GPa at –200V), and at the same time slightly further enhances the density of the coating and the hardness.

References


