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Characterization of magnetron sputtering TiB_2 and Ti-B-N thin films①

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[Abstract] TiB_2 and Ti-B-N films on various substrates were synthesized using ionized dc-magnetron sputtering. A two-turn coil powered by 13.56 MHz r.f. was used to enhance the ionization fraction of the plasma. The structure and properties of the films are affected by several parameters such as substrate bias, total pressure and nitrogen partial pressure and by the substrate materials. The crystallinity and the hardness of the films increase with decreasing total pressure. Well crystallized TiB_2 films with strong (0001) texture and with hardness up to 50 GPa were produced. Nitrogen doping into TiB_2 films decreases their crystallinity and hardness. About 1 GPa residual compressive stress was determined by a wafer curvature technique. It was performed that the dry friction of several different hard films against hardened 52100 steel, which showed the TiB_2 and Ti-B-N films existing the lowest friction coefficient and the lowest wear rate.

[Key words] TiB_2 and Ti-B-N coating; dc-magnetron sputtering; residual stress; mechanical properties; tribology
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1 INTRODUCTION

Wear and corrosion cost a lot of materials every year all over the world and degrade productivity and reliability. It is always a great attention to investigate hard coatings to protect the surface of tools and components from wear and corrosion. Some ultrahard coatings like diamond or cubic boron nitride have been prepared. However, the adhesion of these coatings is too low for mechanical applications[1].

Titanium diboride and titanium boron nitride coatings have attracted attention in recent yeas due to their combination of high hardness and stiffness and excellent chemical stability[2~4]. It has been shown that they are favorable to be used in erosive, abrasive, corrosive and high temperature environment[5,6]. They have been synthesized by a wide range of deposition techniques such as PACVD[7], arc PVD[8], PES[6], IP[9], sputtering and co-sputtering[1], and so on. It was reported that the hardness of the coatings is degreased when nitrogen is incorporated into TiB_2 coatings[2,5]. Other results indicated, however, doping nitrogen can improve hardness and tribological properties of the coatings, if the nitrogen content is limited in some range[1,10,11]. Some papers[11,12] reported that the phase composition of the films can be indicated by the Ti-B-N ternary phase diagram, though the deposition condition is far from thermodynamical equilibrium. On the contrary, Ref. [1] emphasized that the crystalline forms of the films do not correspond to these indicated in the Ti-B-N phase diagram.

In this work, a wide range of deposition parameters are tested to verify the structure and properties of the films, and it's related to the deposition condition.

2 EXPERIMENTAL

An ionized magnetron sputtering system[13] was used in this study. A titanium diboride target was mounted on the cathode. A substrate holder was located 7.5 cm below the target. The cathode and the chamber were cooled by flowing water. Between the target and the substrate there was a two turn water cooled copper coil, which was powered by 13.56 MHz r.f. power adjusted by a T-shape matching network. Argon or argon-nitrogen mixtures were used as the working gas, the nitrogen flow was controlled using a MKS flow controller connected to a MKS 147 multi-gas controller. The total pressure was maintained at a constant value by a closed loop control system using a MKS Baratron pressure gauge. The substrate was biased negatively, with a 30 kHz pulsed-dc, in order to control the ion bombardment of the substrate surface. A wide range of processing parameters is tested in this work. The base chamber pressure was 4×10^{-3} Pa. The substrate temperature was measured using a calomel-alumel thermocouple set deep inside the

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graphite substrate holder. The substrate temperature was less than 200 ℃ during deposition.

Polished Si(100) wafers, stainless steel, M1 steel and glass slides were used as substrate. The substrates were cleaned sequentially with acetone and methanol in an ultrasonic bath. Sputter-etching in an argon plasma at 1.1 Pa with 25 W r.f. power and -500 V substrate bias was performed for 5 min to remove any residual pollution or surface oxides.

A Dektak 3030ST surface texture analysis system was used to measure the film thickness. And the curvatures of Si wafer before and after coating deposition were measured using this system to estimate the residual stress of the coatings[14]. The microstructure was studied by X-ray diffraction spectra (XRD). The hardness of the films was measured by a Vickers and an ultra-microindentation system with a Berkvich indenter. The adhesion/cohesion was estimated using LSRH scratch tester. The tribological test was performed on a block-on ring tester with a 52100 steel (R=19 mm) ring rotates, dry-milling against a coated stainless steel sample. The sliding speed was 0.12 m/s, the normal load was 0.5 N and the Hertzzian stress was about 95 MPa.

3 RESULTS AND ANALYSIS

3.1 Structure analysis

The effect of deposition pressure on the TiB_2 film (coated on stainless steel) structure is clearly illustrated in Fig.1. It can be seen that a perfect hexagonal crystalline with very strong (0001) texture was synthesized at a total pressure of 0.67 Pa. By increasing the total pressure from 0.67 to 2.67 Pa, the structure of the film changed gradually from strong (0001) textured crystalline to an almost amorphous with some disordered crystals (besides the (0001) peak, there are $(10\bar{1}0)$, $(10\bar{1}1)$ peaks as seen in Fig.1(c)). This change results in a great difference in hardness of the films, which will be discussed later.

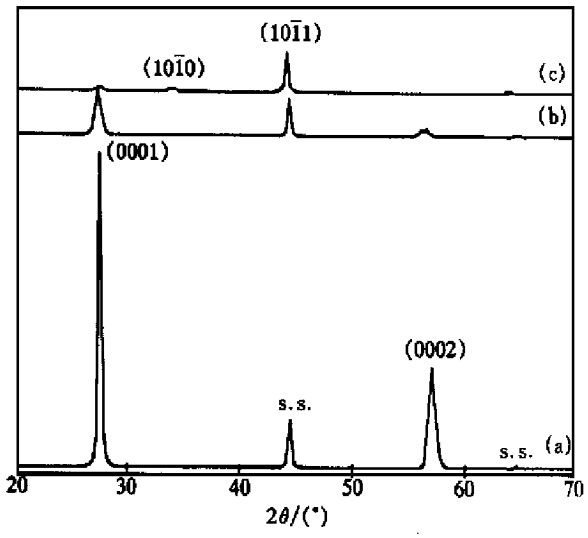


Fig.1 XRD patterns of TiB_2 films prepared at different total pressures
(Target power=350 W, Sub. bias=-80 V, r.f. power=25 W)
(a) —0.67 Pa; (b) —1.33 Pa; (c) —2.67 Pa

The substrate bias controlled ion bombardment effectively during deposition[12], which affected the microstructure of the film. In this study, when the bias was less than -30 V or more than -200 V, the film was almost amorphous no matter how much the deposition pressure was. The most suitable bias voltage for favorable crystallization is in the range of -80 V to -100 V in this system.

Mixing nitrogen into the deposition gas resulted in decreasing crystallinity of the film. As shown in Fig.2(a), when doping small nitrogen gas, there is only a weak (0001) peak of TiB_2(N) compared with a strong and sharp (0001) peak of TiB_2 in Fig.1(a).

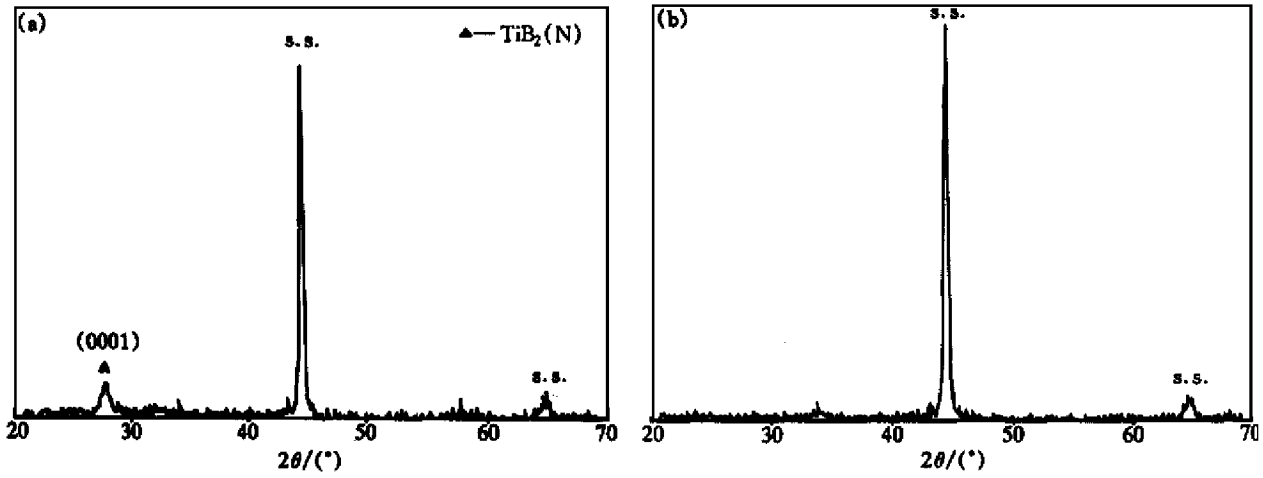


Fig.2 XRD patterns of Ti-B-N films (Target power=300 W; Sub. bias=-100 V; p_t=0.67 Pa)
(a) —$p(N_2)$=0.067 Pa; (b) —$p(N_2)$=0.080 Pa

There is no peak anymore with increasing nitrogen flow rate further as indicated by Fig .2(b) . Although the peak of TiB_2(N) is weak , it enhanced the hardness of the Ti-B-N film markedly , which will be shown later .

The structure of the film is affected by substrate materials . The structures of the coatings on Si(100) wafers and glass slides are almost amorphous in this work .

3 .2 Hardness and adhesion analysis

Fig . 3 shows that the correlation between the hardness and the deposition pressure of two series of TiB_2 films . The deposited condition is given below the Fig . 3 . Both curves show the same correlation : the hardness of the film decreases with the total pressure increasing . This hardness variation with gas pressure is due to the structure changes as mentioned above . With increasing total pressure , the structure of the film transformed from (0001) textured well-crystallized to disordered worse-crystalline and at last to almost amorphous . Meanwhile , the hardness of the film decreased from 44 GPa to 27 GPa (series(a)) and then to 19 GPa (series(b)) . Besides the structure , the deposited stress also affects the hardness , which will be discussed later .

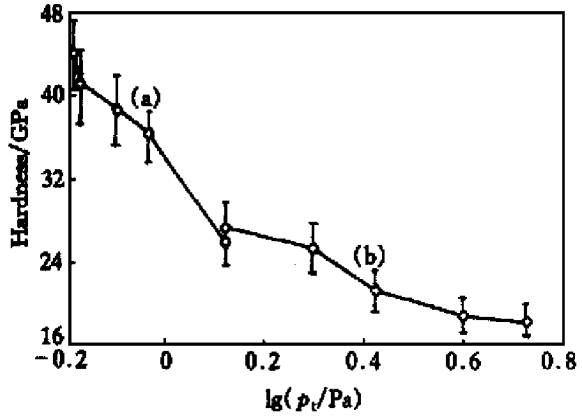


Fig .3 Hardness vs total pressure
(a) —Target power = 350 W; Sub . bias = - 80 V;
r.f. power = 25 W;(b) —Target power = 300 W;
Sub . bias = - 100 V; r.f. power = 0

It seems , however , that the hardness of the film is independent of r.f. power in this study . This is consistent with the previous work[13] .

Another two series of TiB_2 films were deposited at various substrate bias voltages . One was deposited at p_t = 2 .00 Pa , the other at p_t = 2 .67 Pa . And the both hold P_{targ} = 300 W and $P_{r.f.}$ = 0 . The hardness of the two series of the films on stainless steel versus substrate bias V_b is shown in Fig . 4 . It indicates , with increasing the bias voltage , the hardness increased quickly and reached the maximum at 25 .6 and 21 .8 GPa respectively at V_b = - 100 V , then decreased gradually with the V_b increasing . This variation is associated with the structure transformation . At V_b = - 100 V , the films have the best crystallinity . Either increasing or decreasing the bias level from - 100 V , results in deteriorating their crystallinity as illustrated before .

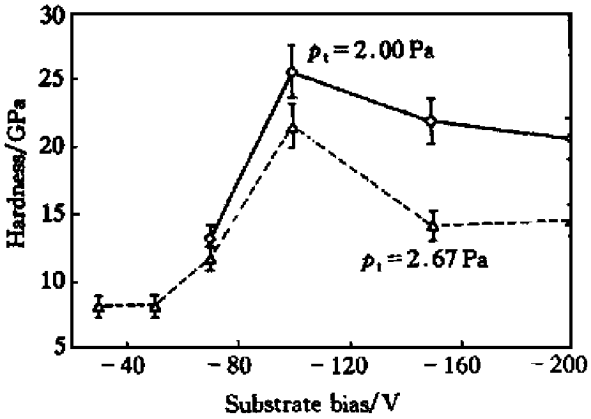


Fig .4 Hardness vs substrate bias
(Target power = 300 W;
r.f. power = 0 ; substrate : stainless steel)

Fig . 5 shows the correlation between the hardness and the nitrogen partial pressure of two series of Ti-B-N coatings . It demonstrates the tendency : doping nitrogen in the sputtering gas decreased the hardness of the films , and with increasing nitrogen partial pressure , the hardness of the films decreased monotonously . This results is consistent with literature [5] . It is interested to note that there is a great difference in hardness between the films deposited with nitrogen partial pressure of 0 .067 Pa and 0 .080 Pa . This is due to the microstructure change between the films as mentioned before .

From Fig . 5 , it can be seen that at any $p(N_2)$, the HV of the films decreases with the p_t increase , similar to the TiB_2 films .

The adhesion of the films on the steels is about 10 ~ 20 N , estimated from the scratch test . But there

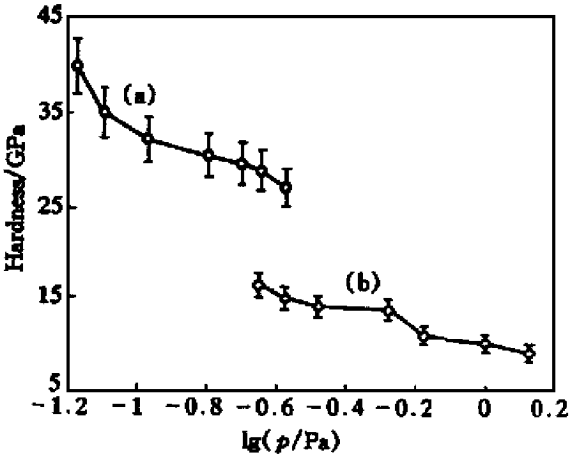


Fig .5 Hardness vs nitrogen partial pressure
(a) —Total pressure = 0 .67 Pa , target power = 350 W ,
sub . bias = - 80 V , r.f. power = 25 W;
(b) —Total pressure = 2 .67 Pa , target power = 300 W ,
sub . bias = - 100 V , r.f. power = 0

is no evident correlation between the adhesion and the deposition condition. This is due to the measuring method. Because the hardness of the substrate is less than 5 GPa, and the hardness of the film generally is more than 20 GPa, but the thickness of the film is only 1 ~ 3 μm. So that the scratch value is affected greatly by the thickness of the film. The thicker the films, the higher the scratch value. This dominant factor conceals other influence factors. The double films enhance the adhesion and hardness greatly, for example, the adhesion of TiN/TiB_2 double coatings reaches 25 N and the hardness is 50 GPa.

3.3 Deposited stress analysis

It is known that the deposited stress (residual film stress) is an important factor which affects the properties of the coatings prepared by PVD[15]. This study used the curvature difference of Si wafer before and after coating deposition to determine the residual stress as mentioned before. The calculating formula was[16]

$$\sigma_f = \frac{E_s}{6(1-\nu_s)} \frac{t_s^2}{t_f}\left(\frac{1}{R_0} - \frac{1}{R}\right) \quad (1)$$

where σ_f is the residual film stress, E_s and ν_s are the elastic modulus and Poisson ratio of the Si wafer respectively, t_s and t_f are the thickness of the Si wafer and the film respectively, and $1/R$ and $1/R_0$ are the curvature of the Si wafer after and before deposition respectively. The $1/R_0$ is about zero as seen in Fig.6(a). E_s = 98 GPa, ν_s = 0.3 are used here. The result is listed in Table 1.

There are four features as seen in Table 1. First, with decreasing the total pressure the compressive stress in the film increases, and the increased compressive stress leads to enhancing the hardness of the film[15]. Unlike previous work[10] which reported that there was a transition from compressive to tensile stress when the total pressure was ranged from 6 to 7 mTorr (0.80 to 0.93 Pa) and power was ranged from 300 to 400 W, in this work the residual stress was all compressive when the deposited total pressure was ranged from 0.67 to 4.0 Pa, with a - 80 to - 100 V and pulsed-dc bias under the power range as the same as the Ref.[10].

Secondly, the residual stress increases as the substrate bias is enhanced, and the compressive stress reaches the maximum when the bias voltage = - 100 V, then it relaxes even transforms to tensile stress when the bias is enhanced further. This transition of the residual stress is coincident with the hardness variety of the films as seen in Fig.4.

Thirdly, increasing the target power results also in enhancement of the residual stress.

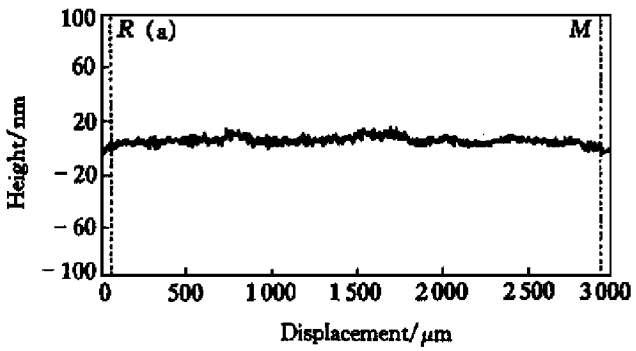
Finally, for nitrogen partial pressure over 0.27 Pa, the residual stress decreases quickly until 0.53 Pa, then it remains almost constant.

3.4 Friction and wear

TiB_2, Ti-B-N and several other materials films deposited on stainless steel were used for tribological

Table 1 Residual stress of films

p_t/ Pa	$p(N_2)$/ Pa	Bias/ V	Power/ W	r.f./ W	σ_f/ MPa
0.65	0	- 80	400	30	- 1 972
0.65	0	- 80	350	30	- 1 872
0.67	0	- 80	350	30	- 1 755
0.80	0	- 80	350	25	- 1 476
0.93	0	- 80	350	25	- 1 338
1.06	0	- 80	350	25	- 1 112
1.33	0	- 80	350	25	- 925
2.67	0	- 100	300	0	- 787
2.67	0	- 70	300	0	- 483
2.67	0	- 50	300	0	- 66
2.67	0	- 30	300	0	0
2.67	0	- 200	300	0	+ 213
4.00	0	- 100	300	0	- 487
2.67	0.27	- 100	300	0	- 768
2.67	0.40	- 100	300	0	- 643
2.67	0.53	- 100	300	0	- 520
2.67	0.67	- 100	300	0	- 551
2.67	1.00	- 100	300	0	- 523
2.67	1.33	- 100	300	0	- 566



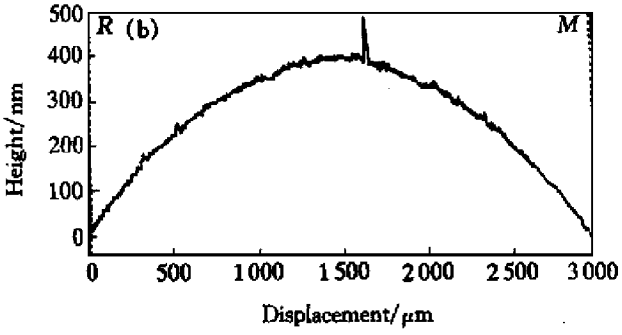


Fig.6 Typical profilometer scanning traces on Si wafer
(a) —Before deposition; (b) —After deposition

studies. The testing for TiB_2 films was performed for 10 min and others were 5 min. The typical variations in coefficient of friction with testing time of the films are shown in Fig. 7. The friction coefficient of the TiB_2 film is about 0.1, and for the Ti-B-N film, it is slightly lower than that for the TiB_2 film within initial 200 s, then it increases and becomes larger than that for TiB_2. A possible explanation is that the Ti-B-N film is softer than the TiB_2 film, thereby the surface of Ti-B-N film becomes rough sooner than the TiB_2 film during tribotesting. The wear volume loss of all films was about a linear function of time within the test period. This is consistent with Ref.[10].

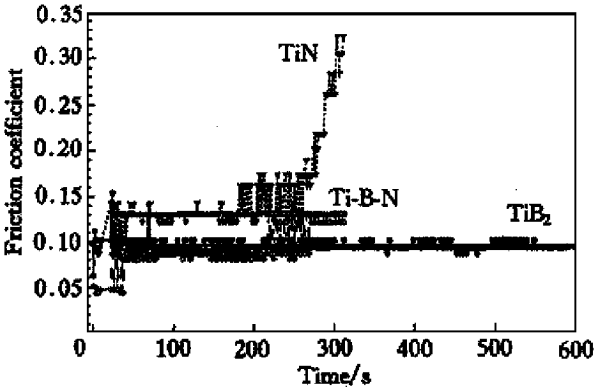


Fig. 7 Variation of friction coefficient testing with time
(Load: 0.5 N; sliding speed: 0.12 m/s; dry sliding in air; substrate: stainless steel)

The comparison of tribological properties of several films is given in Table 2. It shows that the TiB_2 and Ti-B-N coatings possess the lowest friction coefficient and the lowest wear rate in all the selected coatings.

Table 2 Comparison of tribological properties of various coatings

Coating	Thickness /μm	Hardness / GPa	Friction coefficient	Wear rate / (10^{-16} $m^3 \cdot N^{-1} m^{-1}$)
TiB_2	1.6	43	0.1	4.5
Ti-B-N	1.6	34	0.09	4.2
TiN	3.0	20	0.14	25.5
BC_x	2.5	20	0.5	140
CrN	3	20	0.5	11
AlN_x/TiN	2.7	19	0.25	12
TiB_2/TiN	1.6/3.0	50	0.1	4.5

4 DISCUSSION

4.1 Crystalline or amorphous

The crystallinity of the films is controlled principally by the deposition pressure and substrate bias level as shown before. From the energy point, the film should be crystalline, if the deposition process is equilibrium. It is well known, however, the process is far from equilibrium. The atoms, sputtered from the target, travel through the working gas plasma region until they condense on the surface of the substrate. The condensed atoms possess a certain energy enabled themselves to overcome potential energy generated by the around atoms, to form the crystalline lattice. The suitable ion bombardment enhances mobility of the atoms, which ensures the crystalline forming easy. With increasing the deposition pressure, the energy of the condensed atoms decreases due to transferred to the gas particles through collision during they travel. If the energy of the condensed atoms is too low to overcome the potential or the bombarding strength is too weak to active the condensed atoms mobile, the atoms will pile up randomly and the film will be amorphous. If the bombarding strength is too strong, however, it will destroy the lattice. In other words, the too strong bombardment rises the energy level of the crystalline and the film will grow in amorphous though it is a metastable phase. Furthermore, the too strong bombardment will sputter the condensed atoms resulting in the film peeling off.

In sum, the structure of the film can be controlled by process parameters, especially by the deposition pressure and the substrate bias. Therefore, in some case the phase composition of the Ti-B-N film may be coincident with the ternary phase diagram as reported by Ref.[11,12]. In general, however, it does not correspond to the phase diagram as indicated by Ref.[1].

4.2 Textured or random

For hexagonal crystalline, the free surface energy of (0001) face is the minimum. If the condensed atom is active, the film will be textured (0001) as shown in Fig.1(a). If the activity of the atoms is insufficient, the crystalline of the film will be deteriorated and the texture will be vanished as shown in Fig.1(c). And the activity of the condensed atoms is controlled mainly by total pressure and substrate bias as mentioned before.

4.3 Influence of substrate materials

The films coated on Si(100) or glass are almost amorphous in this study. It may be explained by the film growth dynamics. The structure of steel substrate is bcc with the lattice parameter $a = 0.2886$ nm. And the lattice parameter a of hexagonal TiB_2 is equal to 0.303 nm. The difference between these two is only 0.014 nm (less than 5%). The film can grow on these substrates epitaxially, so the free energy of the system maintains the minimum. On the contrary, the difference of lattice parameters between Si and TiB_2 is larger (more than 22%) and the glass is amorphous, so there is a greater potential barrier for the condensed atoms to form a lattice. It results in

growth in amorphism as we observed.

5 CONCLUSIONS

The present study demonstrates that the TiB_2 and Ti-B-N thin films can be deposited on different substrates using an ionized magnetron sputtering techniques. The structure and the hardness of the films have a strong correlation and can be adjusted by deposition conditions. When the total pressure is ranged from 0.67 to 1.06 Pa, the substrate bias from -80 to -100 V and the target power from 300 to 400 W, well crystallized TiB_2 films with strong (0001) texture, about 1 GPa compressive stress and hardness up to 50 GPa can be obtained. Doping nitrogen into TiB_2 films destroys their crystalline structures and decreases the hardness. But if the nitrogen composition is very small, the hardness of the film is still more than 40 GPa and some hexagonal crystalline TiB_2(N) solid solution is found. The films on steel substrate exhibit low friction coefficient and high wear resistance. These results indicate that the TiB_2 and Ti-B-N films are excellent wear-resistant coatings for tribological application.

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