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Microstructure, mechanical and tribological properties of TiN/Mo_2N nano-multilayer films deposited by magnetron sputtering

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ABSTRACT

TiN/Mo_2N nano-multilayer films with modulation period ranging from 3 nm to 9.8 nm were deposited by magnetron sputtering. TiN and Mo_2N monolithic films were also deposited for comparison. It was found that the (200) preferred orientated TiN/Mo_2N nano-multilayer films exhibited fcc structure similar to B1-NaCl and formed isostructural superlattice with well defined interfaces between TiN and Mo_2N layers. The multilayer films with modulation periods $\lambda = 3$ nm and 5.7 nm exhibited superhardness with a value of about 41 GPa. Both the coefficient of friction and specific wear rate of multilayer films increased from 0.29 to 0.44 and 5.8×10^{-17} m^3/Nm to 1.3×10^{-16} m^3/Nm, respectively, with the increase of the modulation period. The TiN/Mo_2N nano-multilayer films exhibited improved mechanical and tribological properties compared to TiN and Mo_2N monolithic films.

1. Introduction

Ti-based transition metal nitride films have been widely studied as protections for cutting and forming tools in the past decades. Numerous researches on TiN/MeN (Me: Cr, Nb, Al, Si, etc) multilayer films have been extensively carried out. The results showed that those TiN/MeN multilayer films exhibited improved hardness and oxidation resistance than that of TiN films as a result of forming multilayer structure with values increased from 22–26 GPa and 500–600 °C to above 35 GPa and 800 °C, respectively [1–6]. Nevertheless, these multilayer films usually showed high coefficient of friction (COF) with values above 0.7, which limited their efficiency on tribological applications because of the excessive thermal load which arose in machining processes like high-speed or dry cutting. Hence, the integration of solid lubrication phase into TiN film would be a suitable route to improve the overall tribological behavior of TiN-based nitride films.

Since intrinsic solid lubricants like MoS_2 and DLC often fail in their tribological effectiveness with increasing temperature due to oxidation [7,8], lubricious oxide materials with easy moveable shear planes, referred to as Magnéli phase, are attracting increasing interest [9]. It has been documented that Mo–N film could form such oxygen-deficient Magnéli phase oxides at elevated temperatures [10,11]. Some studies performed on TiMoN films showed their excellent mechanical and tribological properties [12,13]. Yang et al. synthesized TiMoN films with different Mo concentrations using dc magnetron sputtering and showed lowered COF to 0.42 and decreased wear rate to 10^{-16} m^3/Nm [13]. However, there have been few studies that reported the effects of the modulation period on the structure and properties of the TiN/Mo_2N nano-multilayer films. Therefore, in this work, TiN/Mo_2N nano-multilayer films with different modulation periods were deposited by magnetron sputtering. The effects of the modulation period on the microstructure, mechanical and tribological properties of the TiN/Mo_2N nano-multilayer films were investigated. These results are also compared to the monolithic TiN and Mo_2N films prepared under similar deposition conditions.

2. Experimental details

TiN/Mo_2N multilayer films were deposited on Si (100) and steel substrates by a closed field unbalanced magnetron sputtering using a Mo target (99.9% purity) and a Ti target (99.99% purity) placed facing and parallel to each other at a distance of 450 mm (the diameter of chamber). The Si wafers and mirror polished steel disks were ultrasonically cleaned in acetone for 15 min and then placed on a rotated sample holder lying in the center of the chamber. After the chamber was evacuated to 2.0×10^{-3} Pa, Ar with the flow rate of 20 sccm was introduced and the substrates were bombarded by Ar^+ ion plasma with a bias voltage of −400 V for 20 min to remove the surface contaminates. A Ti adhesion layer with a thickness of about 50 nm was firstly deposited on the substrates. And then, a mixed TiN_x and MoN_x graded layer with a thickness of about 130 nm was synthesized on the top of titanium layer by gradually increasing nitrogen flow rate and target current to the values which were listed in Table 1. Finally, the TiN/Mo_2N multilayers with the same modulation ratio (η, defined as the ratio of Mo_2N layer thickness to TiN layer thickness) and different modulation periods (λ) were deposited by changing the target currents of Ti and Mo targets proportionally. A nitrogen flow rate of 22 sccm, a bias voltage of −65 V and a rotation speed of 5 rad/min for the sample holder were applied

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Table 1
The deposition and structural parameters of as-deposited films.

Sample ID	Target current (A)		Layer thickness (nm)		Modulation period λ (nm)	Film thickness (μm)
	Ti	Mo	TiN	Mo_2N		
TM-1	2.1	1.7	1.2	1.8	3.0	1.3
TM-2	4.4	3.2	2.3	3.4	5.7	1.2
TM-3	5.4	4.9	3.9	5.9	9.8	1.2
TiN	3 × 2	N/A	N/A	N/A	N/A	1.4
Mo_2N	N/A	3 × 2	N/A	N/A	N/A	1.3

for the deposition of multilayers. The titanium nitride monolithic film and molybdenum nitride monolithic film were also fabricated for comparison by using two Ti or two Mo targets, respectively.

The crystal structure of the as-deposited films was analyzed by a glancing angle X-ray diffractometer (XRD-7000S, Japan) using Cu-Kα radiation in θ–2θ geometry, which was operated at 40 kV and 40 mA. The scanning was performed from 20° to 80° with a speed of 10°/min. The cross-section morphology of the films was observed by JEM-3010 type transmission electron microscopy (TEM). The modulation periods and thickness of as deposited films measured from the TEM images were also summarized in Table 1. Nano-indentation tests were performed to evaluate the hardness and elastic modulus of the films using a Berkovich diamond indenter in the XP-type Nano-Indenter. The indentation depth of 100 nm was controlled less than 1/10 of the film thickness to eliminate the effect of substrate on the film properties [14]. Ball-on-disk (BOD) tests were carried out to study the tribological behavior of the films at room temperature. The carbide ball (WC–6%Co) with a diameter of 5 mm was used as the counterpart and the applied load was kept at 2 N with a sliding speed of 0.28 m/s. The sliding times were regulated at 1800 s, corresponding to a distance of about 540 m. Based on the wear track depth and width measured by the LEXT OLS 4000 Laser Measuring Microscope, the specific wear rate was obtained by normalizing the wear volume with the total sliding distance and the applied load. The wear debris was also studied using an EDS attached in the JSM-6700F scanning electron microscope (SEM).

3. Results and discussion

3.1. Microstructure

The X-ray diffraction patterns of TiN/Mo_2N multilayer films with different modulation periods are presented in Fig. 1. TiN and Mo_2N monolithic films are also introduced for comparison. In the XRD patterns of TiN and Mo_2N films, diffraction peaks observed at the angle around 36.5°, 42.3° and 62.5° can correspond to (111), (200) and (220) of fcc TiN and Mo_2N phases. TiN film grows strongly in (111) preferred orientation while Mo_2N film orients in both (111) and (200) textures. By contrast, all of the TiN/Mo_2N multilayer films exhibit a small difference in XRD patterns and a (200) preferred orientation with texture coefficient TC (200) $\geq$ 1.2. This different film growth compared to TiN and Mo_2N films could be attributed to the lower strain energy density of (200) grains compared to that of (111) grains, which provided a sufficient driving force for the preferential growth of (200) grains [15]. Although (111) and (220) diffraction peaks of multilayer films shift about 1.5° to lower diffraction angles compared to monolithic films, the peak shift values are only about 0.2° for dominant (200) diffraction peaks, which means that the TiN/Mo_2N multilayer films can also be indexed as fcc structure similar to B1-NaCl.

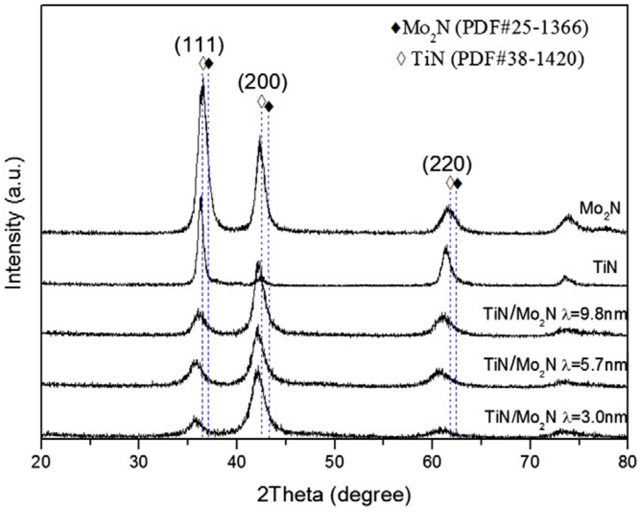

Fig. 1. X-ray diffraction patterns of TiN/Mo_2N nano-multilayer films compared with TiN and Mo_2N monolithic films.

It can also be observed from Fig. 1 that diffraction peaks of TiN and Mo_2N monolithic films shift to lower diffraction angles compared to that of bulk TiN (JCPDF#38-1420) and Mo_2N (JCPDF#25-1366), indicating the increase of lattice parameters. One of the most possible reasons for the increase of lattice parameters is that over-stoichiometric or gas-rich TiN and Mo_2N films were formed, which was a common phenomenon caused by high N_2 partial pressure in reactive magnetron sputtering [16]. The excess N in over-stoichiometric TiN or Mo_2N films would fit into the space between the lattices forming interstitial solid solution and thus expanding the lattices.

The microstructure of the TiN/Mo_2N nano-multilayer films was studied using the TEM. Fig. 2 shows the cross-sectional TEM micrograph of TiN/Mo_2N nano-multilayer films with modulation period $\lambda = 5.7$ nm. TiN/Mo_2N nano-multilayer films exhibit a distinct modulation layered structure with well-defined and abrupt layer interfaces perpendicular to the growth direction (white arrows in Fig. 2). The dark and bright layers in the micrograph correspond to Mo_2N and TiN layers, respectively, since the scattering factor of Ti is lower compared to that of Mo. The modulation period measured from the TEM micrograph is about 5.7 nm, which consisted of TiN layer with a thickness of about 2.3 nm and Mo_2N layer with a thickness of about 3.4 nm. Accordingly, the modulation ratio (η, defined as the ratio of Mo_2N layer thickness to TiN layer thickness) of TM-2 is about 1.5. As the target currents of Ti and Mo are changed proportionally, the modulation ratio of the TiN/Mo_2N nano-multilayers are all kept at about 1.5. The ring featured selected area electron diffraction (SAED) patterns as inserted in Fig. 2a confirmed that the TM-2 is fcc polycrystalline structured, in which the cubic (111), (200), (220) and (311) reflections can be identified.

The microstructure of the interfaces between TiN and Mo_2N layers was further examined by the high-resolution TEM (HRTEM) as shown in Fig. 2b. The lattice fringes generally paralleled to the film growth direction and crossed the layer interfaces for several modulation periods. Hence the TiN and Mo_2N layers could form the isostructural superlattice. The lattice spacing measured from TiN layer and Mo_2N layer as marked in Fig. 2b is 0.2079 nm and 0.2105 nm, respectively. Several dislocations (in the white rings in Fig. 2b) could be clearly observed mainly in Mo_2N layers. These dislocations caused lattice distortion by the localized strain fields in the lattice, which accounts for the formation of internal stress in films [17].

3.2. Mechanical properties

Indentation hardness and elastic modulus of the TiN/Mo_2N nano-multilayer films compared with TiN and Mo_2N monolithic films are shown in Fig. 3. The hardness and elastic modulus of TiN/Mo_2N multilayer films were maintained in high values of about 41 GPa and 400 GPa at modulation periods $\lambda = 3$ nm and 5.7 nm. With the modulation period increased to 9.8 nm, the values decreased a little to 37 GPa and 372 GPa. In comparison with the hardness of TiN and Mo_2N monolithic films, a hardness enhancement of about 10 GPa has been achieved.