

Effect of Nitrogen Flow Rate on Structure and Adhesion Strength of Magnetron Sputtered Ti-Si-N Nanocomposite Films

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Abstract. Ti-Si-N nanocomposite films were prepared by co-sputtering Ti and Si targets in Ar/N₂ gas atmosphere. The effect of N₂ flow rate on the structure, adhesion strength and friction coefficient of the deposited films was studied by using X-ray diffraction, atom force microscope, field emission scanning electron microscopy and multi-functional tester for material surface properties. The Ti-Si-N films had a fine, smooth and compact structure with TiN nanograins embedded in an amorphous Si₃N₄ matrix. The nanocomposite films exhibited (200), (111), (220) and (222) reflections with a dominant orientation of the (200) reflection. When the N₂ flow rate increased, the film structure was refined. It was found that both interfacial adhesion strength and friction coefficient depended on the N₂ flow rate, and the best values were exhibited by the nanocomposite film produced at N₂ flow rate of 15 sccm, perhaps contributed to a finer and smoother structure of this deposited film.

Keywords: Ti-Si-N, Sputtering, Nanocomposite film, Microstructure, Adhesion strength, Friction coefficient

1 Introduction

Titanium nitride is one of the most used materials as hard films because of its high hardness, wear resistance and chemical stability [1]. These films are generally prepared by magnetron sputtering and arc ion plating. The mechanical properties of TiN thin films can be improved through alloying TiN with C, B or Al, Zr etc [2]. Since Veprék [3-5] obtained the Ti-Si-N nanocomposite films via chemical vapor deposition with a hardness of 105 GPa, Ti-Si-N nanocomposite films have been paid much attention [6-10]. Zhang et al [6] prepared nc-TiN/a-SiN_x nanocomposite films with hardness about 40 GPa through reactive magnetron sputtering. Zhou et al [7] reported Ti-Si-N nanocomposite film had a maximum hardness of 47 GPa. In reactive sputtering processes, the microstructure and properties of the Ti-Si-N nanocomposite films strongly depend on the processing parameters such as bias voltage, nitrogen partial pressure, substrate temperature and the content of silicon [7-10]. Because

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relative less information about effect of N₂ flow rate on adhesion strength and friction coefficient of Ti-Si-N nanocomposite films, in this paper Ti-Si-N nanocomposite films were prepared by co-sputtering Ti and Si targets in Ar/N₂ gas atmosphere, and the effect of N₂ flow rate on the microstructure, adhesion strength and friction coefficient of the deposited films was investigated in details.

2 Materials and methods

The Ti-Si-N nanocomposite films were deposited on polished AISI 304 stainless steel substrate with dimensions of 25 mm×25 mm× 2 mm by co-sputtering Ti and Si targets in Ar/N₂ gas atmosphere using reactive magnetron sputtering. Pure Ti (99.99 %) and Si (99.999 %) targets of diameter 60 mm and thickness 4 mm were mounted about 80 mm below the substrate. The base pressure of the deposition chamber was pumped to 6.0×10^{-4} Pa and the process pressure was fixed at 1.9 Pa. High purity Ar (99.999 %) and N₂ (99.999 %) gases were used. Ar gas flow rate was fixed at 10 sccm while N₂ gas flow rate was changed during deposition. The substrates were cleaned and in-situ sputter etched for 15 min in a pure Ar atmosphere before deposition. The current applied on Ti target was 0.2 A (DC), and the RF voltage on Si target was 100 V. The bias voltage applied was -120 V, the depositing temperature and time was 300 °C and 30 min, respectively.

The crystal structure was analyzed by X-ray diffraction (XRD, PANalytical B.V. X Pert Pro MPD) with a Cu-K_α 40 kV/40 mA X-ray source (wavelength $\lambda=0.154056$ nm) at a low incident angle of 2° and in the scanning angular (2 θ) range from 20° to 90° at 2°/min. The surface morphology and roughness of the deposited films were measured by atomic force microscopy (AFM, Agilent 5500) in tapping mode, and the surface and cross sectional morphology was observed using field emission scanning electron microscopy (FESEM, S4800, Hitachi) operated at 3-5 kV voltage. The film/substrate adhesion strength was measured by scratch test, and the friction coefficient was evaluated by reciprocating friction method with MFT-4000 multi-functional tester for material surface properties (Lanzhou Institute of Chemical Physics Chinese Academy of Sciences).

3 Results and discussion

The XRD patterns of the Ti-Si-N thin films deposited at different N₂ flow rate are shown in Fig.1. The diffraction peaks of TiN (B1 NaCl-typed structure) and stainless steel occur in the XRD patterns, and no crystalline TiSi and Si₃N₄ are found. The diffraction peaks of TiN phase are contributed to (200), (111), (220) and (222) crystallographic planes, and a dominant orientation of the (200) plane is exhibited. For TiN the surface energy for the (111), (200) and (220) planes are 400, 230 and 260 J.m⁻², respectively [11]. The (200) plane is the plane of the lowest surface energy in the TiN crystal. Therefore, when the surface energy is the main drive force the TiN crystallites orient on (200) plane. Because the Ti-Si-N films are very thin, the substrate underneath the films could be detected. Because Si₃N₄ phase could be formed under the present preparation conditions, no XRD signals corresponding to crystalline Si₃N₄ phase mean that Si₃N₄ is amorphous. The amorphous Si₃N₄ encapsulates the growing TiN crystallites, preventing their growth [5].

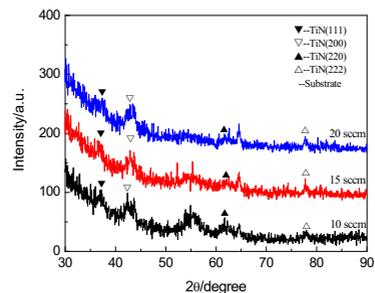


Fig.1 XRD patterns of the Ti-Si-N nanocomposite

Fig.1 also reveals that the intensities of (111) and (220) diffraction peaks of TiN crystallites gradually decrease when the N₂ flow rate increases. Meanwhile, the (200) diffraction peak of TiN broadens with increasing N₂ flow rate. These results above show that the increase in N₂ flow rate is beneficial for the grain refinement of TiN in the nanocomposite film. This may be because increasing N₂ flow rate can result in more a-Si₃N₄ formed [9], inhibiting the growth of TiN grains [5].

The average grain size can be estimated by the Debye–Scherrer formula:

$$D=K\lambda/(\beta\cos\theta) \quad (1)$$

Where K is a constant (K=0.91), D is the mean crystalline dimension normal to diffracting planes, λ is the X-ray wavelength, β in radian is the peak width at half-maximum height and θ is the Bragg's angle. The calculated grain sizes of the TiN crystallites based on the (200) plane diffraction peak according to formula (1) are 6.4 nm, 4.5 nm and 4.6 nm for the N₂ flow rates of 10, 15 and 20 sccm, respectively. All the average grain sizes are fairly small and the film deposited at higher N₂ flow rate has the finest structure. Zhang [12] reported the average grain size of sputtered TiN film produced under a similar condition was 10.4 nm, larger than that of the TiN in the Ti-Si-N nanocomposite films in the present study, showing the preventing grain growth from the amorphous Si₃N₄ is obvious.

AFM surface morphologies of the Ti-Si-N nanocomposite films deposited at different N₂ flow rate are shown in Fig.2. When the N₂ flow rate is lower (at 10 sccm), a small quantity of amorphous Si₃N₄ phase is formed due to less N particles in ionization gas, and they may not effectively encapsulate TiN grains, weakening the refining effect to some extent. As a result, the structure is a little larger. The root mean square roughness (RMS) is 2.21 nm. When the N₂ flow rate increases to 15 sccm, more amorphous Si₃N₄ can be formed, resulting in enhancing grain refinement effect. The RMS is 2.53 nm. However, when the N₂ flow rate reaches to 20 sccm, the film surface is fine, but its RMS reaches to 3.47 nm. Although the RMS gradually increases with increasing N₂ flow rate as shown in Fig.2d, it is still very small, showing the film has a smooth surface.

Fig.3 presents the FESEM surface and cross sectional morphologies of the deposited film produced at N₂ flow rate of 15 sccm, showing that the film is fine, smooth, dense and compact with a columnar structure. Our experimental results show that the thickness for the nanocomposite films deposited at different N₂ flow rate is approximately 167-175 nm, almost independent of the N₂ flow rate [13].

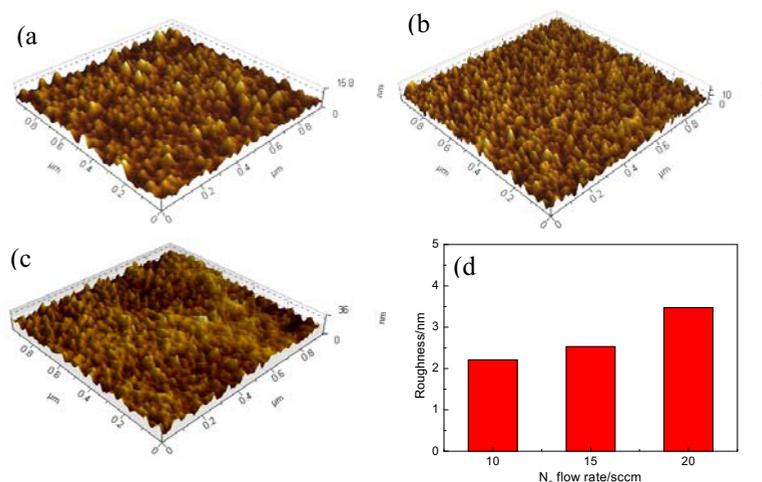


Fig.2 AFM 3D-morphologies roughness of Ti-Si-N nanocomposite films deposited at different N₂ flow rate. (a) 10 sccm, (b) 15 sccm, (c) 20 sccm, (d) roughness

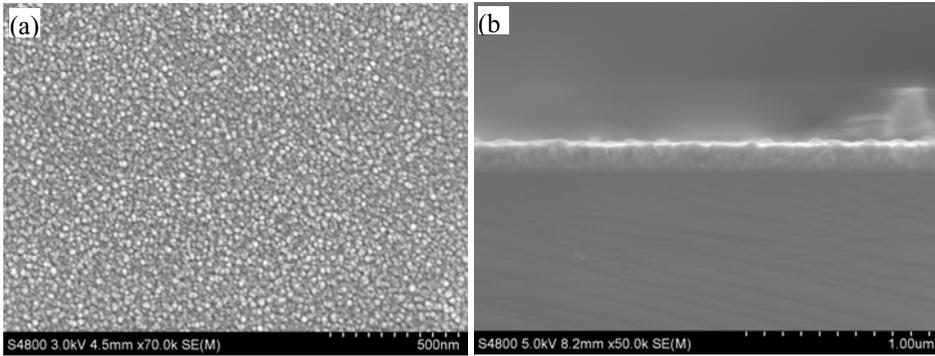


Fig.3 The FESEM surface (a) and cross sectional (b) morphologies of the nanocomposite film produced at N₂ flow rate of 15 sccm

The film/substrate adhesion strength is usually measured through scratch test, it is expressed by the critical load i.e. the lowest pressure force inducing the adhesive failure. Variations of acoustic emission signal intensity with load force applied on the Ti-Si-N film/AISI 304 system during scratching are shown in Fig.4. When the N₂ flow rate is 10, 15 and 20 sccm, the film/substrate adhesion strength is 52, 56 and 37 N, respectively. The adhesion strength first increases and then decreases as the N₂ flow rate increases, and it reaches a maximum value at N₂ flow rate of 15 sccm. This is associated with the finer and smoother structure of the nanocomposite film produced at 15 sccm as shown in Fig.2b and Fig.3a. The excellent adhesion strength of such film may play a positive role in the cutting performance [9]. The film produced at N₂ flow rate of 20 sccm has the lowest adhesion strength, perhaps resulting from its most amorphous Si₃N₄ and highest brittleness [7, 9].

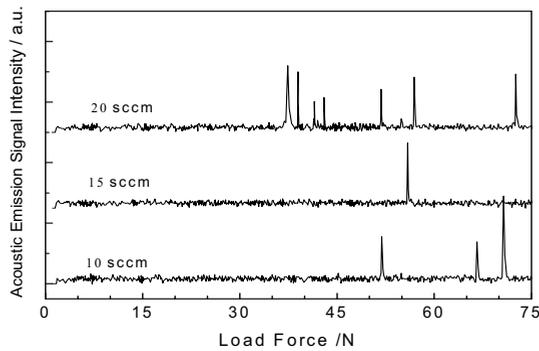


Fig.4 Variation of acoustic emission signal with N₂ flow rate during scratching.

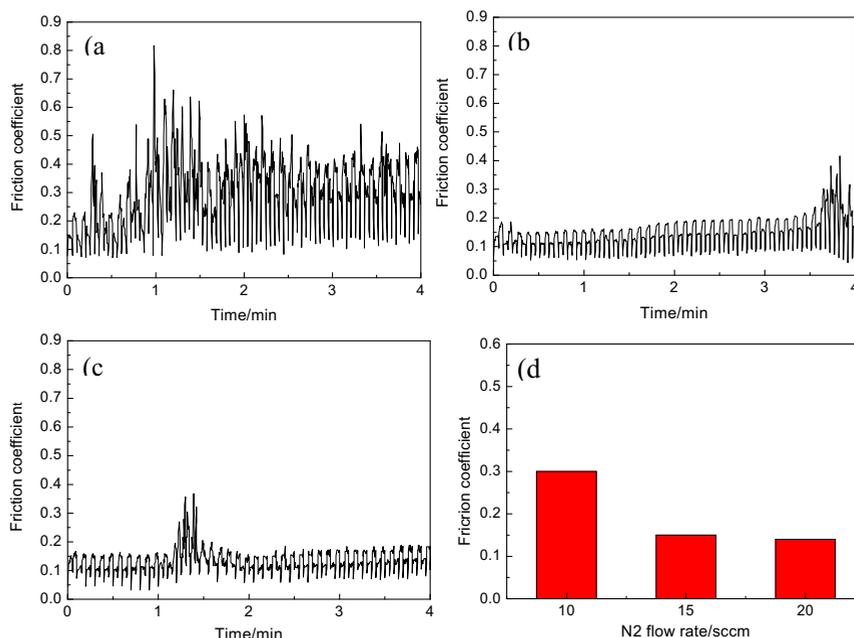


Fig.5 Variations of friction coefficient of the Ti-Si-N films fabricated at different N₂ flow rate.

(a) 10 sccm, (b) 15 sccm, (c) 20 sccm, (d) comparison of friction coefficient.

Variations of friction coefficient of the Ti-Si-N nanocomposite films with friction time measured by reciprocating friction method using Si₃N₄ ball as a counterpart material are shown in Fig.5. When the N₂ flow rate is 10, 15 and 20 sccm, the average friction coefficient of the Ti-Si-N nanocomposite films is 0.30, 0.15 and 0.14, respectively. The friction coefficient is very small and decreases as the N₂ flow rate increases. In fact, it almost does not change when the N₂ flow rate exceeds 15 sccm (Fig.5d). This is associated with the finer structure of the nanocomposite film produced at higher N₂ flow rate.

4 Summary

Ti-Si-N nanocomposite films were deposited at different N₂ flow rate by co-sputtering Ti and Si targets in Ar/N₂ gas atmosphere. The deposited films possess nc-TiN/a-Si₃N₄ nanocomposite structure, and exhibit (200), (111), (220) and (222) reflections with a dominant orientation of the (200) plane. The Ti-Si-N nanocomposite films are fine and smooth with a columnar structure. When N₂ flow rate increases, the grain size of the deposited films gradually decreases whereas the RMS slightly increases. However, the film thickness is almost independent of the N₂ flow rate. The scratch tests show that the adhesion strength first increases and then decreases as the N₂ flow rate increases, and its maximum value is 56 N for the film produced at 15 sccm, contributed to its finer and smoother structure. The friction coefficient of the deposited films is very small and decreases as the N₂ flow rate increases.

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