Influence of N₂ partial pressure on mechanical properties of (Ti,Al)N films deposited by reactive magnetron sputtering

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ABSTRACT

The influence of the nitrogen partial pressure on the mechanical properties of (Ti,Al)N films deposited by DC reactive magnetron sputtering using a Ti–Al mosaic target at a substrate bias of −100 V is investigated. Nanoindentation tests reveal that with increasing N₂ partial pressure, the film hardness and elastic modulus increase initially and then decrease afterwards. The maximum hardness and elastic modulus are 43.4 GPa and 430.8 GPa, respectively. The trend is believed to stem from the variations in the grain size and preferential orientation of the crystals in the (Ti,Al)N films fabricated at varying N₂ partial pressure. The phenomenon is confirmed by results acquired using glancing angle X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS).

1. Introduction

TiN films have been widely used in cutting tools and forming tools for their high hardness and good wear resistance. However, in applications requiring elevated temperature, TiN can be oxidized forming rutile TiO₂ which degrades the mechanical properties of TiN film considerably. In order to improve the mechanical properties and anti-oxidation properties of TiN coatings, a third element (Al, Si, Cr or Zr element) is frequently incorporated to form a ternary composite. Al is one of the most attractive elements. (Ti,Al)N films have been prepared by a number of techniques including ion chemical vapor deposition, ion plating and reactive magnetron sputtering. Reactive magnetron sputtering is one of the most commonly used techniques to prepare (Ti,Al)N films but generally requires a composite target or dual sources to provide the required atoms. A Ti–Al composite target has two main types: alloy and mosaic. An alloy target which is prepared by casting and powder metallurgy techniques has a fixed atomic ratio of Al to Ti whereas a mosaic target is made by embedding Al blocks into the Ti substrate. One of the advantages of a mosaic target is that the atomic ratio of sputtered Al to Ti can be conveniently controlled by changing the surface ratio of Al in the Ti target. In addition, various sputtering parameters such as power, gas pressure, and substrate bias voltage can influence the composition and properties of the deposited film. In this work, the effects of the N₂ partial pressure on the mechanical properties of (Ti,Al)N films deposited by reactive magnetron sputtering using a mosaic target are studied and discussed.

2. Experimental details

The (Ti,Al)N films were deposited by direct current (DC) reactive magnetron sputtering using a mosaic target with an Al (99.999%) to Ti (99.99%) of 1–3. The substrates were M2 high speed steel with dimensions of 15 mm × 15 mm × 4 mm. The samples were mechanically polished, followed by ultrasonic cleaning in acetone and alcohol before introduction into the vacuum chamber. The base pressure in the vacuum chamber was lower than 3.0 Pa. Prior to deposition, the samples were cleaned by 20 kV Ar ion bombardment for about 10 min to remove the oxide. The samples were kept at room temperature and then rotated towards the magnetron sputtering source. The distance from the target to the substrate was about 60 mm. In order to enhance adhesion between the (Ti,Al)N film and the substrate, a Ti–Al interlayer was first deposited. Firstly, only Ar was bled into the chamber to a working pressure of 2.0 Pa and the sputtering time was about 5 min. The deposited Ti–Al buffer layer was about 150 nm thick. Finally, the (Ti,Al)N film was deposited after Ar and N₂ were introduced into the chamber to a pressure of 2.0 Pa and the sputtering time was about 60 min.
with a substrate bias of −100 V. Different film compositions were obtained by altering the N2 and Ar partial pressure.

The film structure was determined by glancing angle X-ray diffraction (GAXRD) using the Cu Kα line, energy of 30 keV, and incident angle of 1°. The composition of (Ti,Al)N was studied by energy dispersive X-ray spectroscopy (EDS). The hardness and elastic modulus values were determined by nanoindentation (CSM) with a Berkovich indenter. The indenter tip shape (area function) was calibrated by indentations on a standard fused silica sample using the method described in Ref. [13]. In nanoindentation test, five locations at least 1 mm apart from each other were randomly selected on each sample. At each location, five indentations were conducted in a line with constant intervals of 10 μm. Thus total 25 indentations were made on each sample to obtain the average properties. The maximum load and indentation depth for each indentation were 10 mN and about 165 nm, respectively.

3. Results

Fig. 1 plots the dependence of the hardness and the elastic modulus of the films on N2 partial pressure. The hardness of the film increases with N2 partial pressure as the N2 partial pressure is varied from 3.4 × 10⁻³ Pa to 33.3 × 10⁻³ Pa. When the N2 partial pressure is 33.3 × 10⁻³ Pa, the maximum hardness of 43.4 GPa is achieved. Further increase of the N2 partial pressure to 40.0 × 10⁻³ Pa reduces the hardness to 41.7 GPa. Similarly, the elastic modulus also increases from 325.1 GPa to 431.8 GPa as the N2 partial pressure increases from 3.4 × 10⁻³ Pa to 33.3 × 10⁻³ Pa and drops to 408.6 GPa when the N2 partial pressure is raised to 40.0 × 10⁻³ Pa.

The XRD patterns in Fig. 2 show a face-centered cubic crystal (f.c.c) structure and the diffraction peaks belong to (111), (200), (220) and (311). With increasing N2 partial pressure, the intensity of the (111) peak decreases but the intensity of the (220) peak increases. (Ti,Al)N films of a strong preferred orientation of (200) were reported in other works [14,15], in which the intensity of (200) and (220) peak are higher than that of (111) in XRD patterns. In this work, with increasing N2 partial pressure the intensity of the preferential orientation (220) peak is much higher than that of (111). It is in good agreement with the studies shown in the literatures [16,17]. This variation in the preferential orientation of the crystals in the (Ti,Al)N films fabricated at varying N2 partial pressure is also related to the substrate materials.

The average crystallite size can be estimated from the full width at half maximum (FWHM) in the XRD pattern using Scherrer’s equation [18]:

\[ D = \frac{K\lambda}{\beta \cos \theta} \]  

where \( D \) is the grain size (nm), \( K \) is Scherrer constant (0.89), \( \lambda \) is the X-ray wavelength, \( \beta \) is FWHM, and \( \theta \) is the diffraction angle. According to Eq. (1) and the FWHM of the (220) peak in the XRD pattern, the grain size of (Ti,Al)N can be estimated. Fig. 3 shows that the grain size decreases with N2 partial pressure as the N2 partial
pressure is varied from $3.4 \times 10^{-3}$ Pa to $33.3 \times 10^{-3}$ Pa. At a N$_2$ partial pressure of $33.3 \times 10^{-3}$ Pa, the grain size reaches the minimum dimension of 12.8 nm. Further increase of the N$_2$ partial pressure to $40.0 \times 10^{-3}$ Pa gives rise to larger grain size.

The EDS results in Fig. 4 show that by increasing the N$_2$ partial pressure, the N content tends to increase while the Al and Ti contents diminish. The composition changes dramatically with the pressure, the N content tends to increase while the Al and Ti contents only diminish slightly from 27.7% to 26.5% and 31.2% to 44.0% as the N$_2$ partial pressure increases from $3 \times 10^{-3}$ Pa to $8.0 \times 10^{-3}$ Pa whereas the Al and Ti contents decrease from 41.3% to 31.5% and 27.5% to 24.5%, respectively. But the change is moderate at high pressure and the ratio of N to (Al + Ti) approaches unity at high nitrogen pressure. For example, as the N$_2$ pressure increases from $18.2 \times 10^{-3}$ Pa to $40.0 \times 10^{-3}$ Pa, the Al and Ti contents only diminish slightly from 27.7% to 26.5% and 23.3% to 22.0%, respectively. Put in the format of Ti$_{1-x}$Al$_x$N, the Al content in the Ti$_{1-x}$Al$_x$N films are varied from $x = 0.600$ to 0.562, 0.543, 0.545 and 0.546 sequentially with increasing N$_2$ partial pressure. In the range of the Al content, the maximum hardness and elastic modulus of the Ti$_{1-x}$Al$_x$N films are obtained. It is in agreement with the report by Han et al. [19]. The hardness of Ti$_{1-x}$Al$_x$N films strongly depends on the Al content of the films and the maximum hardness of the films is noted at an Al/Ti atomic ratio of 11:10.

### 4. Discussion

The nanoindentation results show that the hardness and elastic modulus of the film increase initially with N$_2$ partial pressure but decrease at high pressure condition. The phenomenon is believed to be due to two factors. Firstly, the grain size in the film is changed by the N$_2$ partial pressure. According to the influence of the N$_2$ partial pressure on the grain size in Fig. 3 and mechanical properties (hardness and elastic modulus) in Fig. 1, decrease in the grain size results in higher hardness and increase in the grain size leads to opposite effects. Therefore, the influence of the N$_2$ partial pressure on the hardness is consistent with the well-known Hall–Petch law which describes that the hardness increases with smaller grain size [20]. Secondly, the microstructure of the film is altered by the N$_2$ partial pressure. With increasing N$_2$ partial pressure, the intensity of the (111) peak decreases but that of the (220) peak increases (Fig. 2). That implies the preferred plane (220) parallel to the plane of the films. As is well-known, hardness is a measure of a material’s resistance to localized plastic deformation, and plastic deformation is the cumulative effect of slip of numerous dislocations. Slip occurs more easily between planes that compose bigger interplaner spacing. Therefore, the slip planes are typically close-packed planes. For f.c.c. crystal structure, the (111) planes are the slip planes, a lower energy is needed by the dislocation motion on the (111) plane compared to other planes such as (220). Hence, the change of preferential orientation from (111) to (220) may lead to the variation of the hardness and elastic modulus of (Ti,Al)N films. In addition, changes of the film composition as shown in Fig. 4 can also lead to changes of the film microstructure and mechanical properties [19,21].

### 5. Conclusion

The N$_2$ partial pressure has crucial effects on the hardness and elastic modulus of (Ti,Al)N films prepared by DC reactive magnetron sputtering using a Ti–Al mosaic target. Both the hardness and the elastic modulus of the film increase from 33.0 GPa to 43.4 GPa and from 325.1 GPa to 430.8 GPa, respectively when the N$_2$ partial pressure increases from $3 \times 10^{-3}$ Pa to $33.3 \times 10^{-3}$ Pa. Further increasing the N$_2$ partial pressure to $40.0 \times 10^{-3}$ Pa reduces the hardness and elastic modulus to 41.7 GPa and 408.6 GPa, respectively. The change in the mechanical properties can be attributed to the impact of the N$_2$ partial pressure on the (Ti,Al)N grain size and structure of the film as verified by the XRD and EDS results.

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