Bias effect on microstructure and mechanical properties of magnetron sputtered nanocrystalline titanium carbide thin films

Huili Wang, Sam Zhang⁎, Yibin Li, Deen Sun

School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

Available online 13 July 2007

Abstract

Nanocrystalline titanium carbide (TiC) thin films were prepared by magnetron sputtering deposition at 473 K. The effect of substrate bias on microstructure and mechanical properties was studied in details using X-ray photoelectron spectroscopy, X-ray diffraction, field emission scanning electron microscopy, indentation and scanning microscratch. The TiC films exhibit a (111) preferential orientation. Substrate bias decreases grain size and deposition rate of the TiC films. The TiC films have columnar structure which becomes finer at high substrate bias. Nanoindentation hardness, Young’s modulus, and toughness of the films are increased as the substrate bias goes up. However, the adhesion peaks at substrate bias of −100 V and drops when bias is increased further.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Substrate bias; Magnetron sputtering; TiC; Mechanical properties

1. Introduction

Ceramic films, such as WC, TiC, TiN, TiAlN, due to their high hardness, elastic modulus and wear resistance, are widely used to increase the cutting efficiency and operational life of cutting tools and the dimensional tolerances of components used in applications such as molds and dies, where wear can often occur. TiC has a relative low density (4.91 g/cm³), very high melting point (\(T_m = 3340\) K), high hardness (\(H_V = 28–35\) GPa), high modulus (410–510 GPa), and good thermal stability [1]. Nanocrystalline TiC or nc-TiC thin films can be grown by chemical vapor deposition (CVD) [2] or more popular, physical vapor deposition (PVD) [3–8]. Among various deposition techniques, magnetron sputtering is a conventional and versatile technique. In order to improve the performance of nc-TiC films, many studies have been conducted to investigate the effects of process conditions, microstructure and hardness on performance. In reactive magnetron sputtering, microstructure can be tailored via ion bombardment to enhance the hardness of nc-TiC. For nc-TiC film, toughness is another important issue which limits the service life of coated components [9]. Unfortunately, the toughness of nc-TiC films has received relatively little attention in the past. In this paper, we will focus on the effect of substrate bias on microstructure and mechanical properties of nc-TiC thin films including toughness.

2. Experimental details

2.1. Film preparation

TiC films were deposited on Si (100) substrate using the E303A magnetron sputtering system (Penta Vacuum). Details of the deposition system were described elsewhere [10]. Graphite (99.999 at.% purity) and titanium (99.99 at.% purity) targets were mounted about 100 mm above the Si (100) substrate. The substrate bias varies from −20 to −200 V. The power densities of graphite and titanium were kept constant at 10.5 W/cm² and 4.3 W/cm², respectively. The base pressure of the deposition chamber was pumped to 1.33 × 10⁻⁵ Pa and the process pressure was kept constant at 0.6 Pa with 50 sccm Ar flow. The substrate was ultrasonically cleaned for 20 min in acetone followed by 10 min ultrasonic cleaning in ethanol and finally 5 min ultrasonic cleaning in deionized water. After loaded, the substrate was heated to 200 °C and maintained for 60 min. Prior to deposition, the substrate was plasma cleaned for 20 min at RF induced bias voltage of 300 V to remove surface contaminants and possible oxides (for example, silicon dioxide).
2.2. Film characterization

The film thickness was measured using profilometer (Dektak 3 SI) through a sharp step made with masking part of the silicon substrate by plastic tape prior to deposition. The atomic concentration of Ti and C was characterized by X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra) with monochromatic Al Kα (1486.71 eV) X-ray radiation (15 kV and 10 mA). To remove the surface contamination layer, Ar ion bombardment was performed at an angle of incidence of 45° with an accelerating voltage of 4 keV. The bombardment was performed at an angle of incidence of 45° with respect to the surface normal. The crystal structure was analyzed using X-ray diffraction (XRD, Philips PW1830) with a Cu-Kα 40 kV/30 mA X-ray source (wavelength λ = 0.15406 nm). The scanning was conducted from 20° to 90° at step size 0.01° and 0.5 s per step.

As a first order approximation, the average grain size was estimated by the Debye–Scherrer formula [11]:

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

(1)

where \( K \) is a constant (\( K = 0.91 \)), \( D \) is the mean crystalline dimension normal to diffracting planes, \( \lambda \) is the X-ray wavelength (\( \lambda = 0.15406 \) nm), \( \beta \) in radian is the peak width at half-maximum height and \( \theta \) is the Bragg’s angle.

The cross-sectional images were observed using field emission scanning electron microscopy (FESEM, JEOL JSM-6340F, Japan).

The hardness and Young’s modulus of the films were determined using MTS Nanoindentator XP with a Berkovich diamond tip and continuous stiffness measurement capability in depth control mode. The hardness and modulus were calculated in the indentation depth of 50 nm (less than one tenth of the film thickness) to minimize the substrate effect. In order to get an accurate area function, the tip area function was calibrated by indenting a standard fused quartz bulk sample.

nc-TiC film toughness was evaluated using indentation method with micro hardness tester (DMH-1) with a Vickers indenter. Indentation was conducted at different loads (from 98 to 9800 mN). For each load, at least three readings were obtained. The toughness \( K_{IC} \) was calculated through [12]:

\[ K_{IC} = \delta \left( \frac{E}{H} \right)^{1/2} \left( \frac{P}{c^{3/2}} \right) \]  

(2)

where \( P \) is the applied indentation load; \( E \) and \( H \) are the elastic modulus and hardness of the coating, respectively. \( \delta \) is an empirical constant which depends on the geometry of the indenter, for Vickers indenter \( \delta = 0.016 \). \( c \) is the crack length which was measured by scanning electron microscopy (SEM, JEOL JSM-5600LV). In order to reduce the substrate effect on film toughness, \( K_{IC} \) calculated from Eq. (1) was plotted versus indentation depth and then the curve was extrapolated to zero indentation depth.

The adhesion strength was studied using the scanning microscratch tester (Shimadzu SST-101) where a diamond tip of 15 μm in radius was dragged on the coating with a gradually increased load. The scanning amplitude was set at 50 μm at a speed of 10 μm/s. Critical load was used to indicate the adhesion strength.

3. Results and discussion

3.1. Deposition rate and chemical composition

The deposition rate (film thickness over deposition time) decreases gradually from 11.3 to 6.8 nm/s when substrate bias increases from −20 V to −200 V. The drop of deposition rate is caused by resputtering of the as-deposited film, i.e., kicking off the adatoms or growing surface by the incoming ions. XPS results show that Ti/C atomic ratio deviates only a little from 1 as the substrate bias increases (Fig. 1). In the case of reactive sputtering, the substrate bias may affect the stoichiometry of TiC film through decomposition of carbon source gas. In our case, however, co-sputtering of titanium and graphite does not significantly affect the composition when substrate bias is varied. Fig. 2(a) and (b) plot the XPS spectra of C 1s and Ti 2p for nc-TiC films at different substrate bias. The peak at the binding energy of 281.8 eV is TiC peak. No peak at about 284.8 eV, i.e. no C–C bond is formed. The Ti 2p3/2 peak of Ti in TiC is at 454.9 eV and that of metallic Ti is at 453.8 eV [13]. The Ti 2p1/2 peak is at 461.0 eV for Ti in TiC and 459.9 eV for metallic Ti [13]. No metallic Ti 2p3/2 and Ti 2p1/2 peaks are detectable. Therefore the structure of the film was virtually 100% TiC.

Therefore we can conclude the composition of the films was stoichiometric TiC.

3.2. Microstructure

Fig. 3 shows the XRD analysis of the films. The peak around 69° is from the Si (100) substrate underneath the film. No peak of Ti or carbon is found. Peaks at 35.9, 41.7, and 76.1° are attributed to (111), (200) and (222) diffraction planes of TiC. All these patterns exhibit relatively broad peaks and have a dominant orientation of the (111) plane. The (111) preferential
orientation is possibly due to the smallest surface energy storage in the stressed state [14]. As a consequence of enhanced mobility of atoms on the growing film surface, the film structure can be relaxed to a lower energy state with the formation of (111) texture.

The calculated grain sizes of the TiC crystallite are listed in Fig. 4. The grain size drops from ~27 to 14 nm as the substrate bias increases. Substrate bias can cause resputtering of species from the growing film surface [6]. The possible reasons are the penetration of impinging ions into the lattice of the condensed film and the increased generation of defects which will lead to an increased number of preferential nucleation sites, resulting in smaller grains.

FESEM micrographs of the cross-sections of the films deposited at different substrate biases are shown in Fig. 5. Substrate bias promotes columnar increase. However, the morphology is finer at higher substrate bias which agrees with the calculated grain size. At bias −200 V, the film has smaller columnar structure compared with the film at bias −150 V. TiC has a melting temperature ($T_m$) of 3340 K [1] while the deposition temperature ($T_s$) is 473 K, giving rise to a homologue temperature $T_s/T_m$ of only ~0.14. Therefore, the TiC film should possess a Zone I (equiaxial small grain) structure, according to the Thornton model [15]. However, at different biases (−20 V to −200 V), the TiC films show a Zone T structure. With a negative substrate bias applied to the substrate, the ionized argon in the plasma will increase. Intense substrate ion bombardment (bias sputtering) can deliver high energy to the depositing film and result in a dense film. The mechanism is primarily a sputter-induced redistribution of coating material.

### 3.3. Mechanical properties

Hardness and Young’s modulus of the nc-TiC films at different substrate biases are shown in Fig. 6. At −20 V bias, the hardness and Young’s modulus of the film are only 13.9 GPa and 208.6 GPa, respectively. At −200 V bias, the hardness and Young’s modulus are improved to 28.8 GPa and 302.5 GPa, respectively. Overall, the hardness and Young’s modulus of the nc-TiC films were enhanced by the substrate bias, in good agreement with grain size refinery. The enhancement of hardness and modulus can be attributed to two aspects. On one hand, the substrate bias promotes the TiC crystallization. On the other hand, the substrate bias intensifies the ion peening effect, resulting in residual stress which may affect the hardness value. It is well known that an internal stress can be induced due...
to the substrate bias (as in the case of TiC films synthesized by a filtered cathodic vacuum arc technique [16] and in the case of sputtered TiN films [17]).

The adhesion strength of nc-TiC films is presented in Fig. 7. At −20 V, the lowest adhesion (58 mN) is obtained. As the bias increases, the adhesion strength reaches the peak value (252 mN) at −100 V. However, further increase of bias leads to the adhesion drop due to the high intrinsic stress caused by ion bombardment.

Table 1 lists the toughness results at various substrate biases. The film deposited at −20 V bias was easily fractured at 98 mN indentation load (the minimum load in our instrument) thus invalid for toughness calculation. While at −200 V bias, the crack load threshold is increased up to 1960 mN, which means the load capacity is heightened. For the film deposited at −200 V bias, the toughness is also improved about 60% compared with that at −100 V. All the toughness data are comparable and falls into the range of ~1–2 MPa m^1/2 which is comparable to the reported bulk indentation toughness value [18].

Higher ion energy can eliminate the shadowing effect which is typical in zone I structure and surface diffusion will dominate. Recently, Pei et al. [19,20] studied the substrate bias effect on nc-TiC/a-C:H coatings prepared by close field unbalanced magnetron sputtering (CFUMS). Increasing bias changed the coating microstructure, and showed clear transition from columnar to glassy microstructure in the nanocomposite layer. Substrate bias...
greatly enhanced coating toughness. The toughness trend indicates the coating with a glassy microstructure exhibiting substantial toughening effects. Ion bombardment can densify the structure and prevent the formation of voids and large columnar boundaries which are detrimental in terms of microcrack initiation and propagation under load. Therefore, in our case, nc-TiC toughness is enhanced partially by the refinery of columnar structure. Another possible contribution to the enhanced toughness is compressive stress [9,21]. Since cracking is generally initiated by tensile stress, compressive residue stress has to be overcome first. Thus compressively stressed films can possess higher toughness than unstressed films.

4. Conclusions

The deposition rate and grain size of sputtered TiC films decrease with increase of substrate bias. The TiC films have (111) preferential orientation. All films have a columnar structure but the column becomes finer at high substrate bias.

The hardness, Young’s modulus, load capacity and toughness of the TiC films are enhanced by substrate bias, but too high substrate bias will lead to the deterioration of adhesion strength. The toughness of the TiC films is 1.19–1.89 MPa m$^{1/2}$, comparable to TiC bulk toughness. The toughness enhancement may be attributed to the compressive stress and restrained columnar growth due to ion bombardment.

Table 1
The crack load threshold and toughness of TiC films at different substrate bias

<table>
<thead>
<tr>
<th>Substrate bias (−V)</th>
<th>Crack load threshold (mN)</th>
<th>Toughness KIC (MPa m$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>≤ 98</td>
<td>–</td>
</tr>
<tr>
<td>100</td>
<td>490</td>
<td>1.19±0.34</td>
</tr>
<tr>
<td>150</td>
<td>980</td>
<td>1.60±0.19</td>
</tr>
<tr>
<td>200</td>
<td>1960</td>
<td>1.89±0.45</td>
</tr>
</tbody>
</table>

References