Deposition of Ti-Al-N Films by Using a Cathodic Vacuum Arc with Pulsed Bias

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Abstract Ti-Al-N hard films have been prepared by cathodic arc deposition by using an unipolar pulsed bias. In the present study, Ti-Al-N films were deposited on stainless steel and silicon wafers. The deposition rate, micrograph, preferred orientation and composition were systematically investigated by using x-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), and a scanning electron microscope (SEM). It is shown that substrate bias duty cycle and frequency have a great effect on film structure. A simple explanation for the results is also presented.

Keywords: cathodic vacuum arc, Ti-Al-N film, pulsed bias

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1 Introduction

Transition metal nitride films such as TiN, ZrN and HfN, which exhibit very high hardness and extreme resistance to wear, have been extensively studied for hard coatings in cutting tools and molding dies. Cathodic vacuum arc (CVA) deposition is the most commonly used method for deposition of group-III nitride thin films. Moreover, the inherent high energy can improve the film pack density and film substrate adhesion. Because of the high degree of ionization achieved in the arc evaporated material, the plasma can be easily controlled using a negative substrate bias potential. Substrate bias is a very important parameter for the deposition. A negative potential applied to the substrate is known to significantly affect the structure, composition and properties of Ti-Al-N films [1]. DING et al. [2] found that increasing the substrate bias from −200 V to −1000 V enhances the internal stress in TiC film.

A recent development in the field of pulsed power is the application of pulsing at the substrate. Pulsed bias in a cathodic arc deposition system has been demonstrated to allow a decrease in the substrate temperature and maintenance of a higher net deposition rate in comparison to conventional DC bias [3]. FRESSMANN et al. [4] deposited TiN and Zr(C,N) using a cathodic arc plasma deposition process with pulsed bias frequencies of 0~25 kHz and observed that substrate temperature can be decreased to as low as 100~150 °C without loss of coating adhesion. TiN was also deposited in a bias frequency range of 10~33 kHz, resulting in a reduction in the average substrate bulk temperature [5]. A similar observation was also made by LUGSCHIEIDER et al. [6] for Ti-Al-N coating deposited with a pulsed bias source. It has been also found that with the pulsed bias, the ion current at the substrate did not saturate and continued to rise with the increase in both bias voltage and bias frequency. Additionally, a fully dense featureless structure of coating has been obtained [7]. COOKE et al. [8] reported numerous advantages of pulsed bias like elimination of substrate arcing, achievement of a given ion current with low operating voltages, more uniform cleaning and more uniform adhesion. An increase in the ion current with substrate bias frequency was also obtained by LEE et al [9].

The present work aimed to obtain further improved performance characteristics by optimizing the pulsed bias. Pulsed bias with different duty cycles and frequencies was applied to deposit Ti-Al-N films on silicon wafers and stainless steel. The microstructure and mechanical properties of Ti-Al-N films deposited with pulsed bias were investigated while keeping other parameters constant during the deposition process. The deposition rate, phase structure, surface and cross-section morphologies, and the mechanical properties were also systematically studied.

2 Experimental details

Ti-Al-N films were deposited on silicon wafers and steel substrates by using the cathodic vacuum arc technique (shown in Fig. 1) in N2/Ar gas mixtures, using a compound Ti(50)%Al(50)% (atomic ratio) target. The arc current for the target was 80 A. As a modification to the original system, a unipolar pulsed bias power supply was used, which provided pulsed voltages in the range from 0 V to −1000 V and frequencies from 40 kHz to 60 kHz. Fig. 2 shows a typical voltage-time diagram of a unipolar pulsed bias. The duty cycle r is the ratio between the time of bias on and the total time of a
pulsed cycle. Charged particles are accelerated to the substrates only when the bias is on.

Stainless steel and silicon wafers with a square of 10 mm × 15 mm were used as substrates. The specimens were ultrasonically cleaned in acetone and then in de-ionized water. Prior to deposition, the chamber was evacuated to a base pressure of 9×10⁻³ Pa, and then Ar⁺ ions were introduced into the chamber to clean the substrates by sputtering. Prior to deposition, ion bombardment was carried out at a substrate bias voltage of −1000 V (40 kHz, r=0.5). A 100 nm thick TiAl layer was deposited as an inter layer between the substrate and the Ti-Al-N film. The process parameters were as summarized in Table 1.

Table 1. Conditions for the Ti-Al-N deposition process

<table>
<thead>
<tr>
<th>Items</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound target</td>
<td>Ti:Al = 50:50 (atomic ratio)</td>
</tr>
<tr>
<td>Total gas pressure</td>
<td>P_g = 1.2 Pa</td>
</tr>
<tr>
<td>N₂ partial pressure</td>
<td>90%</td>
</tr>
<tr>
<td>Clearing time</td>
<td>60 min</td>
</tr>
<tr>
<td>Ion bombardment</td>
<td>−800 V, 5 min</td>
</tr>
<tr>
<td>Deposition time</td>
<td>40 min</td>
</tr>
<tr>
<td>Voltage of bias</td>
<td>−100 V</td>
</tr>
<tr>
<td>Duty cycle of bias</td>
<td>0.3, 0.5, 0.7</td>
</tr>
<tr>
<td>Frequency of bias (kHz)</td>
<td>40, 50, 60</td>
</tr>
</tbody>
</table>

The microstructure, morphology and thickness of the films were determined by measuring the surface and cross-section of the films with a field-emission SEM coupled with an energy dispersive X-ray analysis system (EDX), operated at a 20 kV voltage. Meanwhile, the deposition rate was obtained by dividing the thickness with deposition time. The phase composition and crystal structure of the as-deposited films were identified by XRD (D/Max-2400) using Cu Kα radiation under 40 kV and 120 mA in a θ-2θ geometry. The nanoindentation tests were performed using a nanoindenter II with a Berkovich indenter tip. The instrument was operated in continuous stiffness mode and the indentations were made using a constant nominal strain rate of 0.05 s⁻¹. Three indentations were made per film.

3 Results and discussion

The effect of the pulsed bias source on the film properties was investigated with different duty cycles while keeping the frequency constant (40 kHz), and in the case when it was studied with different frequencies, the duty cycle was kept constant (0.5). The applied bias voltage and gas pressure during the deposition were −100 V and 1.2 Pa for all deposited films.

The dependence of the deposition rate of Ti-Al-N films on the substrate bias is presented in Fig. 3. Fig. 3(a) shows that the deposition rate decreases from 21 nm/min to 11.5 nm/min with the increase of the duty cycle. The increase of the duty cycle could make specimens attract more ions, and enhance ion bombardment. So the coating was resputtered by ion bombardment, which reduced its thickness. The influence of the frequency of applied pulsed bias on the deposition rate is shown in Fig. 3(b). The maximum of the deposition rate (21 nm/min) was achieved for the films deposited at the frequency of 50 kHz. The slight difference in the coating thickness was due to the different frequencies of pulsed bias.
a −100 V bias voltage are shown in Figs. 4 and 5. Granular structures were found in each coating. Based on the thickness of Ti-Al-N films, as measured in Figs. 4 and 5, the deposition rate is plotted in Fig. 3. From Fig. 3 we find that the frequency and duty cycle of the substrate bias are significant factors for the deposition rate. It is argued that the increasing ion impingement and channeling/respattering effects on the growing films with a pulsing frequency and duty cycle were responsible for the decreased deposition rate. Generally, a higher bias voltage is in favor of sputtering rather than deposition. When the bias voltage was applied between the substrates and chamber, most of it dropped in a narrow space near the substrate. The distance d, which represented the distance from the substrate to the point of ground potential, was approximately 1 mm and was related to the pressure and bias voltage [10]. A variable frequency may cause the changes in d. The mechanism of this narrow range oscillation is very complicated. Under a pulsed bias, it may have an influence on the deposition rate [11].

The XRD patterns of Ti-Al-N films deposited under different bias duty cycles and frequencies (bias voltage: −100 V) are shown in Fig. 6. The (100), (111) and (220) reflections can be observed from two figures. It is obvious that the crystallographic structure of the Ti-Al-N films is affected by the duty cycle (Fig. 6(a)). However, the structure is less influenced by the frequency of the pulsed bias (Fig. 6(b)). The preferred orientation of (220) showed a dependence on the duty cycle. Though the preferred orientation of Ti-Al-N film was (100) at r=0.3, increasing the duty cycle caused the texture to shift gradually from (111) to the (220) preferred orientation. In the Ti-Al-N films, the Ti atoms in TiN lattice were replaced by Al atoms. The difference in the atom radius caused a strong solution, which led to a distortion of the lattice. The solution strength would enhance the hardness of the film at a higher Al content. The peak width of textured grains in the growth direction (111) was very narrow, indicating a high degree of crystallinity [12].

The results of the Al content measured by energy-dispersive X-ray (EDX) analysis are shown in Table 2. The maximum Al content was found for the films with r=0.3 duty cycle. The Al content decreased in the films, which could be attributed to the difference in the ionization degree of Ti and Al. The ionization degree of Ti vapor was higher (80%) than for Al vapor (50%).
Thus, Ti ions were preferentially attracted to the negatively biased specimen, altering the final Al/(Ti+Al) ratio. With the increase in the duty cycle and frequency of the bias, the ion bombardment also caused a loss in the Al content. Fig. 7 shows the nanohardness of the films under different duty cycles and frequencies. It was not strongly influenced by the duty cycle or the frequency, especially at a lower bias voltage (−100 V). We can obtain that there was only a slight tendency of increasing nanohardness for deposition with a pulsed bias source. However, with an increasing bias voltage, the influence of the pulsed bias on the nanohardness became stronger. It is suggested that a high bias voltage creates strong ion bombardment and will result in a change in microstructure and better film uniformity.

4 Conclusion

In the present research, Ti-Al-N films have been deposited on stainless steel and silicon wafers by using a pulsed bias cathodic vacuum arc. The effect of the duty cycle and frequency on the microstructure and properties of Ti-Al-N films has been investigated. Based on the experimental results, the following conclusions can be made:

a. The deposition rate and cross-section micrograph are very dependent on the bias duty cycle and frequency while the pressure and bias voltage are kept constant. The deposition rate of the films decreases with the increase in the duty cycle and frequency.

b. The preferred orientations of Ti-Al-N (220) and (111) show dependence on the duty cycle, but are less influenced by the bias frequency. The cross-section SEM images show a dense and homogeneous multi-layer structure of the Ti-Al-N films.

c. The highest hardness of Ti-Al-N films is 36 GPa. With the variance of the bias duty cycle and frequency, the nanohardness is only slightly different because of a low bias voltage (−100 V). The ideal mechanical properties of the films are obtained while the duty cycle and frequency are 0.5 kHz and 60 kHz, respectively.

References


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