Influence of negative bias voltage on microstructure and property of Al-Ti-N films deposited by multi-arc ion plating

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Abstract

In this study, we systematically investigated the effects of negative bias voltage on the composition, deposition efficiency, microstructure, and mechanical properties of multi-arc ion plated (MAIP) AlTiN films. The films were deposited on high-speed steel substrates by MAIP at various negative bias voltages. The results indicated that the Al content [$Al/(Al+Ti)$ ratio] and the deposition efficiency were significantly altered by the application of negative bias voltages. X-ray photoelectron spectroscopy analysis showed that the AlTiN films were composed of Ti-N and Al-N bonds. The macroparticles (MPs) on the film surface decreased with increasing negative bias voltage. We also discussed the different types of MPs found on the films and their influence on the process of determining the hardness of the films. The microhardness of the films depends on the negative bias voltages. The films deposited at -250 V exhibited a maximum hardness of ~45 GPa. The adhesion and frictional tests revealed that the film deposited at -150 V demonstrated the highest cracking resistance, the best adhesion under a critical load of 78 N, highest adhesion strength, and the lowest and stablest coefficient of friction at 0.23.

Keywords: Thin films; Ion plating; Indentation (normal, micro, and nano), Adhesion; X-ray photo-emission spectroscopy (XPS)

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1. Introduction

TiN and TiN-based films are widely used as protective material for cutting tools, molds, and mechanical components in many industries [1, 2]. Among these films, TiAlN films are increasingly drawing attention because of their superior hardness, advanced wear, and oxidation-resistance properties compared with conventional binary transition-metal nitride films, such as TiN and CrN [3]. The TiAlN films used for industrial applications can be fabricated using various physical vapor deposition techniques, such as magnetron sputtering [4], cathodic-arc evaporation [5], ion-beam sputter deposition [6], and hybrid coating techniques.

The microstructures and compositions of TiN and TiN-based films vary depending on the degree of control on deposition parameters, such as substrate temperatures, gas pressures, target powers, and bias voltages. Thus, these factors ultimately determine the performance of the films [2-10]. The bias voltage is a very important parameter in arc ion plating (AIP) deposition. AIP can produce nitride-based coatings with high hardness and excellent adhesion at high deposition rates by varying the bias voltages applied to the substrate, thereby changing the ion energy bombardment and further influencing the nucleation and growth kinetics during film deposition. Thus, with such changes, the properties of the films are greatly modified.

TiAlN films with different microstructures and compositions have been widely investigated in previous studies with respect to their preparation method and mechanical properties [2-10]. Kale et al. [10] reported that Al concentration decreased with increasing bias voltage and that the h-(Ti, Al)N phase exists at lower bias voltages. Zhou et al. [4] found that, with increasing nitrogen partial pressure, the intensity of the preferential orientation (220) peak is much higher than that of (111), thus producing maximum hardness and elastic modulus of 43.4 and 430.8 GPa, respectively. The results are attributed to the smaller grain size and higher energy needed to initiate the (220) plane compared with that needed to initiate the (111) plane.

Increasing the nitrogen partial pressure by reducing both the degree of predominance in the (200) plane and the crystallinity of films resulted in increased electrical resistivity [6]. Compared with single TiAlN coatings, graded and multilayered TiAlN coatings exhibited excellent machining performance, which may be ascribed to their lower residual stress and higher thermal stability [2, 5]. Developing ceramic coatings with sufficiently high hardness and improved toughness remains a challenge. Aside from the sophisticated microstructures and compositional designs of the films, high hardness and improved toughness can also be achieved through post-treatments, such as heat treatments. Yang et al. [11] attained high adhesion strength in films by decreasing the average residual stresses after vacuum at temperatures ranging from 200 °C to 500 °C. Stable hardness at high temperatures and improved plasticity can also be obtained by annealing within the temperatures ranging from 700 °C to 800 °C for 2 h in vacuum, thus improving the interrupted turning and end-milling performance of the cutting tools [3]. Endrino et al. [12] pointed out that the lower adhesion tendency of the workpiece material and better chip formation conditions can be achieved if the Al-rich TiAlN coating is annealed under an oxygenic atmosphere at 700 °C because the post-treatment causes the formation of an outer composite amorphous alumina–titania layer.

However, information on the generation of macroparticles (MPs) and their influence on AlTiN films, especially on hardness, are lacking. In the present study, we investigated the influence of negative bias voltage on the composition and structure of AIP AlTiN films and discussed the generation of MPs and their effect on the hardness of the films. The influence of negative bias voltage on adhesion and coefficient of friction was also investigated.

2. Experimental

AlTiN films were deposited on high-speed steel (HSS) substrates and Si wafers using an industrial cathode arc plasma deposition equipment. Two sources, one fitted with a titanium cathode (diameter of 100 mm) and the other with an

aluminum–titanium cathode (Al 67 at.%, Ti 33 at.%, diameter of 100 mm), were installed facing each other on each side of the chamber wall. Substrates were mounted on a twofold rotating turntable to provide homogeneous films in the growth. The shortest cathode-to-substrate distance was 70 mm.

HSS substrates (4 mm × Φ 12 mm) were polished to a surface roughness of 0.02 μ m (Ra) using 1.0 μ m alumina suspension. The HSS substrates and Si wafers were ultrasonically cleaned for 10 minutes in acetone and alcohol, respectively. The deposition chamber was evacuated to a base pressure of 7.0×10^{-3} Pa. The substrates were sputter-cleaned in argon plasma for 15 minutes using a bias voltage $V_b = -1000$ V. The high-purity working gas Ar (99.999% purity) and the reactive gas N₂ (99.999% purity) were injected near the substrate. The Ar and N₂ inlet fluxes were fixed to deposit the films at a N₂ partial pressure of 1.2 Pa. The substrates were exposed to bias voltage in the range of -70 V to -250 V. The arc current for both the titanium and aluminum–titanium cathodes was 55 A. TiN was first deposited for 30 minutes, serving as a buffer layer. The Al₆₇Ti₃₃ target was ignited to co-deposit the AlTiN transition layer, which was also considered an AlTiN layer with low Al content. The AlTiN transition layer was co-deposited for 22 minutes. Finally, the Ti target was closed, and the AlTiN layer, which was considered an AlTiN layer with high Al content, was deposited for 39 minutes.

A Bruker D8 advance X-ray diffractometer (XRD) in θ – 2θ configuration with Cu K α radiation operated at 40 kV and 30 mA was used to determine the phases of the films. The scanning step and scanning speed were 0.01° and 4 °/min, respectively. The cross sections of the specimens were observed using a field emission scanning electron microscope (FE-SEM; FEI NANOSEM 430). The thickness of the samples was determined by FE-SEM and using ball-cratering tests. The thicknesses of the samples deposited at -70, -150, and -250 V were 2.03, 1.42, and 1.27 μ m, respectively. Scanning electron microscopy (SEM) was used to observe the surface morphology of the films. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250) was performed to observe the bonding states and chemical contents of the films. Before the XPS experiment, the films were sputter-cleaned in Ar plasma for 5 minutes. The

X-ray source adopted monochromatic Al-K α ($h\nu=1486.6$ eV) with 150 W, and the XP spectra obtained were calibrated using carbon peak C1 s at 284.8 eV. Given a low detection depth of about several nanometers, only the surface element concentrations were examined by XPS (oxygen was excluded in this paper). Energy diffraction spectrum (EDS) technology was used to examine the overall element concentrations of the films. The element concentrations obtained were calibrated using a Mn standard sample. The collection time for each spot was about 30 s to 60 s, and the acceleration voltage was 15 keV. Surface optical microscopy images were also investigated using a Zeiss Axiophot metallurgical microscope to collect macroparticle statistics. A computer-controlled nanoindenter (MTS, Nanoindenter XP) equipped with a Berkovich diamond indenter was used to measure the hardness and elastic modulus of the films. The adhesion strength of the deposited films was evaluated using a standard Rockwell indentation tester and scratch test. Tribological tests were performed with a ball-on-disk rotating-type friction tester at room temperature to evaluate the tribological properties of AlTiN films. The friction pair used was WC-Co balls. The friction test time and relative humidity were 32 minutes and 67%, respectively.

3. Results and Discussion

3.1 Chemical composition and deposition efficiency of Al-Ti-N films

Fig. 1 shows the effect of negative bias voltage on Al content [$Al/(Al+Ti)$], which depended entirely on the bias voltage. Based on Fig. 1(d), Al content invariably decreased from 51.9% at -70 V, to 50% at -150 V, and to 40.4% at -250 V with increasing negative bias voltage. The XPS analyses reveal the composition of AlTiN film deposited at -70 V was 28 at.% Al, 26 at.% Ti, and 46 at.% N. For the film deposited at -150 V, the chemical composition was 29 at.% Al, 29 at.% Ti, and 42 at.% N. For the film deposited at -250 V, the chemical composition was 23 at.% Al, 34 at.% Ti, and 43 at.% N. Thus, all the AlTiN films were substoichiometric, with

$([\text{Ti}]+[\text{Al}])/[\text{N}]$ ratios ranging from 1.17 to 1.38. The compositions of the AlTiN films as shown by EDS were also presented. The conditions that possibly caused the changes in Al content include the following:

(1) Different ionized fractions, namely, 80% Ti and 50% Al. The highly ionized Ti ions were preferentially attracted to negatively biased substrates, causing the Al/Ti ratio in the films to deviate from the nominal 0.667 of the $\text{Al}_{67}\text{Ti}_{33}$ target [13];

(2) Resputtering generated by negative bias. Al atoms in the growing film were preferentially resputtered over Ti atoms because Al is lighter than Ti, resulting in decreased Al content with increasing bias voltage;

(3) Change in Al content also influenced by the charge state distribution (CSD) of the ions in the ion flux. In this study, Ti and Al exhibited mean charge states of +2.1 and +1.7, respectively [14]. During film deposition, the ions with higher CSDs bombarded the surface with higher energies and penetrated deeper into the film subjected to negative bias voltage. Thus, with increasing negative bias voltage, the preferential resputtering of Al atoms with lower CSDs occurred, and the film yielded a higher Ti concentration with a higher CSD. Therefore, the reduction in Al content was the hybrid effect mentioned above. The preferential resputtering caused by the bias can also change the microstructure and properties of the films by changing their element contents. Previous studies have reported similar results for N and Si in CrSiN, which significantly changed the microstructure of the film during film growth [15, 16].

The deposition rate of AlTiN films as a function of bias voltage is illustrated in Fig. 2. The deposition rate showed a decreasing trend within the range of -70 V to -250 V and obtained a maximum value of 22.3 nm/min at -70 V. With increasing bias voltage, the resputtering effect caused by ion bombardment decreased the deposition rate.

3.2 Film microstructures analyzed by XPS and XRD

Figs. 3(a) and 3(b) show the XP spectra of the AlTiN films deposited at -70 and -150 V. No remarkable differences were observed among the films deposited under

different negative biases. The Al 2p peak deconvolution indicated that, for AlTiN films, the peak is composed of two components. The characteristic peak at the binding energy of 74.1 eV corresponded to Al-N bonds, whereas the peak at the binding energy of 73.2 eV corresponded to Al-Ti bonds in complex nitrides [9]. In the Ti 2p spectra, the metallic hcp-Ti film exhibited two characteristic peaks at the binding energies of 453.8 and 459.9 eV, corresponding to the 2p_{3/2} and 2p_{1/2} electrons, respectively [17]. In the present study, the binding energies of 454.8 and 460.6 eV were considered as the Ti2p_{3/2}-N and Ti2p_{1/2}-N peaks, respectively. The peak at the binding energy of 456.7 eV corresponded to Ti-Al bonds in complex nitrides. The N 1s peak was resolved into one component at 396.8 eV, which is consistent with the Ti-N bonds and with one component at 396.5 eV from Al-N bonds, which are in close agreement with the previously reported values of 396.5 eV for AlN and 396.7 eV for TiN [18, 19]. The XPS results confirmed that the Ti atoms in TiN with NaCl in the structure were substituted by Al atoms that bonded to N atoms to form AlN, thus resulting in a solid solution (Al, Ti)N phase.

Fig. 4 presents the typical XRD patterns of Al-Ti-N films under various negative bias voltages. The main phase was a face-centered cubic (fcc) AlTiN with diffraction peaks of (111), (200), and (222), which were identified within the range of -70 V to -250 V. However, the (200) and (222) peaks with very weak intensities at -70 and -150 V completely disappeared at -250 V. Previous studies have reported that (111) and (200) are the main orientations in TiN- and TiN-based films, and the presence of mixed (111) and (200) orientations is the result of the competitive growth between the surface and strain energies [1, 20, 21]. The (200) orientation with a minimum surface energy was expected when the films were deposited at a low thickness. With further increases in thickness, the strain energy became dominant, and a (111) orientation was expected accordingly [22].

3.3 Cross-sectional morphologies

The FE-SEM cross sections of the films with various bias voltages are shown in Fig. 5. The pronounced columnar growth of AlTiN films was observed under SEM in

previous studies, where the columnar units grew outward from the film–substrate interface and throughout the entire film layer [7]. The columnar growth during film deposition was closely related to the deposition parameters. Shetty et al. [23] found that columnar growth is related to the deposition angle and deposition temperature. They pointed out that, with increasing deposition temperature, the films deposited under normal circumstances exhibited distinct faceted crystallites, whereas the oblique angle-deposited (OAD) films developed a kind of “tiles of a roof” or “stepwise structure” with no faceted crystallites. The OAD films showed an inclined columnar structure, with columns tilting in the direction of the incident flux.

3.4 Surface topography and macroparticles

Fig. 6(a) shows the typical SEM image of an AlTiN film deposited at -150 V. Many MPs with diameters measuring hundreds of nanometers to a few microns formed on the film surface. The EDS results showed that the MPs [Fig. (6b)] contained more Ti than the rest of the film [Fig. (6c)], indicating that the MPs were rich in Ti. Figs. 7(a) to 7(c) show the optical micrographs of AlTiN films deposited at various bias voltages. In this study, the MPs either came from the droplets emitted by arc spots in the Ti and AlTi targets or resulted from the collision of an excess of atoms or ions from targets during interaction with the substrates, in which the atoms or ions collided with one another and agglomerated into MPs with the ensuing energy loss. Wang and Kim [24] classified MPs into solid and liquid droplets according to the state in which the MPs were deposited on the substrate. The MPs were classified into three types according to how the MPs formed on the films (Fig. 8): (1) MPs developed at the film–substrate interface and throughout the entire film, similar to the columnar growth of the film; (2) MPs developed inside the film and terminated in the interior or on the film surface; and (3) MPs formed exclusively on the film surface.

The MP density of AlTiN films as a function of various negative bias voltages is plotted in Fig. 9. In this study, MP density is defined as $f_{MPs} = \frac{A_{MPs}}{A_{total}}$, where A_{MPs} and A_{total} are the area of all MPs in a photo and the total area, respectively. The MP density decreased with increasing bias voltage. The MP density initially underwent a

rapid decrease from 0.232 at -70 V to 0.143 at -150 V and then showed a slight decrease as the bias voltage further increased to -250 V. The decrease in MP density with increasing bias voltage showed that an increase in bias voltage exhibits a filtration effect on the MPs. Previous investigations [24, 25] have demonstrated that the MPs on the film surface were filtered by applying negative DC and pulsed biases. Two main theories were proposed to explain the MP filtration mechanism. The first theory is ion bombardment mechanism, which refers to the collision between the incident ions and the growing film, resulting in the removal of loosely bonded MPs. The kinetic energy of the incident ions was proportional to the bias applied to the substrates. Thus, the greater the bias, the more apparent the ion bombardment effect will be. The second theory is electrical repulsion theory [26]. The conditions, $Q_p U_{\text{bias}} > \frac{1}{2} M_p v_p^2$, should be fulfilled, where U_{bias} is the bias voltage and v_p , M_p , and Q_p are the velocity, mass, and charge of the MPs, respectively. In moving towards the substrate, the MPs collected more electrons and became negatively charged because of inevitable random collisions with electrons, ions, or neutral atoms, which are MPs subsequently absorbed by the MPs. Repulsion from the electric field in the near-substrate sheath was the main reason for the filtration of MPs. The effect of repulsion from the substrate on the MPs strongly depended on the negative bias voltage, the charges of the ions, and the current density in the sheath. Fig. 9 shows that the MP density slightly decreased with further increase in negative bias voltage, indicating that the filtration effect becomes saturated when the bias reaches a certain critical value, for example, -150 V in this study. Fig. 7 also demonstrates that the filtration effect on larger-sized MPs ($d > 2 \mu\text{m}$) decreased to minimum levels with increasing bias. Similar results were also reported in the literature [24]. We conclude based on the analysis of the experimental results that the MP filtration by negative bias voltage was the hybrid effect of ion bombardment and electrical repulsion.

3.5 Hardness measured by nanoindentation tests

Fig. 10 shows the load displacement data for AlTiN films deposited at various negative bias voltages, from which the hardness was deduced by employing the

Oliver and Pharr analysis[27, 28]. All the load-displacement curves exhibited similar features. With respect to all the curves within the 50 nm to 400 nm range, we observed that the load applied to the films can be ranked as $-250\text{ V} > -150\text{ V} > -70\text{ V}$, indicating that the film deposited at -250 V possessed the maximum hardness, followed by the films deposited at -150 and -70 V , respectively. For the thickness of all films within the range of $1.27\text{ }\mu\text{m}$ to $2.03\text{ }\mu\text{m}$, the obtained results were credible. The hardness vs. displacement curves derived from the load-displacement data of the films as a function of bias voltage are presented in Fig. 11. For each curve, the hardness values were intensively displacement dependent.

The hardness displacement curves were divided into three stages: increasing stage, platform stage, and down stage [29]. For the first stage, the hardness rapidly increased at a shallow depth. In this step, the rapid increase in H -value was due to the influence of the surface roughness and elastic deformation of the films. The second stage was the platform stage, which showed the combined effect of elastic deformation and plastic deformation. The H -value obtained in this stage was considered as the actual hardness of the films because hardness is defined as the resistance of a material to local plastic deformation, and plastic deformation contributes most to hardness measurements. In the third stage, given the influence of a softer substrate, the H -value gradually decreased and approached a constant value with further increase in indentation depth.

The depths of the platform, which were influenced by the hardness, thickness, and surface morphologies of the films, varied with bias voltage. For the film deposited at -250 V , the film depth at which the maximum hardness was obtained was around 65 nm . The depth increased to about 100 and 140 nm with further decrease in the negative bias from -150 V to -70 V , respectively. However, the hardness for the film deposited at -70 V rebounded at $>190\text{ nm}$ depth. The results obtained from the hardness-displacement curves were consistent with those obtained from the load-displacement curves.

Studies have focused on measuring the hardness of films, but the validity of the process of determining the hardness of the films remains controversial because the

process is influenced by many intrinsic and external factors [30, 31]. According to the concept proposed by several researchers, the d/h ratio, where d and h are the indentation depth and thickness of the film, respectively, should be less than 0.1 to avoid sustaining the influence of softer substrates. In this study, the d -values were considered as the indentation depths for the film that produced the maximum hardness, and h was measured using the ball-erosion test. All the d/h values of the films were less than 0.1. The h -value can be determined more accurately by considering the film hardness to avoid the effect of size indentation effect and the influence of the substrates. Taking the film deposited at -150 V, for example, its average hardness of 42 GPa in the range of 58 nm to 160 nm can be considered as the film hardness.

The hardness and elastic moduli of the AlTiN films as a function of bias voltage is plotted in Fig. 12. With increasing bias voltage, the hardness and elastic moduli of the films increased and reached the maximum values of 45 and 712 GPa, respectively, at -250 V. Thus, the hardness and the elastic moduli of the films are dependent on deposition parameters, such as the negative bias voltage. Although quantifying the residual stress in the film with increasing bias voltage is difficult, previous investigations have shown that AlTiN films with Al content ranging from 40% to 60% exhibit a higher compressive stress [32, 33]. With increasing bias voltage from -70 V to -150 V, the hardness of the film increased from 28 GPa to 38 GPa, which may be due to the residual stress generated by ion bombarding. Another likely explanation for this phenomenon is the spinodal decomposition of fcc-(Al, Ti)N into fcc-(Al, Ti)N/fcc-AlN due to the local fluctuations of the Ti and Al concentrations in AlTiN, which are controlled by both the bias voltage and Al content [33]. In this study, the higher bias voltage of -150 V possibly enhanced the spinodal decomposition of fcc-(Al, Ti)N, which increased the hardness. With increasing bias voltage up to -250 V, the spinodal decomposition becomes saturated and the bias voltage largely loses influence on the spinodal decomposition. Thus, the high hardness of 45 GPa at -250 V may be related to the high-energy ion bombardment caused by the overlarge bias voltage, which would result in higher-density lattice defects.

MPs classified as coating defects are typically incorporated into thin films

deposited by AIP and are typically a few microns in diameter [34, 35]. These defects were confirmed as liquid MPs because they were primarily spherical in shape and rich in Ti, as revealed by EDS. These softer metallic MPs are undesirable because they cause film performance to deteriorate and influence the valid hardness measurement of the films, resulting in a drastic fluctuation in hardness. As shown in Fig. 14, several MPs are visible in the indentation sites.

Fig. 13 shows the influence of different types of MPs on the load displacement curves for the AlTiN film deposited at -150 V. Curve *d* showed a trend different from those of curves *a*, *b*, and *c*, indicating that the load applied on the *d* indentation site was lesser than that applied on any of the other three indentation sites. The loads were ordered as $c < b < a$ at a depth < 1400 nm.

The effect of different types of MPs on the hardness-displacement curves of the AlTiN film deposited at -150 V is shown in Fig. 14. Curve *a* showed the typical hardness displacement curve when no more MPs were available in the indentation sites. Curve *b* exhibited a rapid decrease at a depth < 34 nm, followed by a rapid increase, obtaining the maximum value of 29 GPa at a depth of about 150 nm. However, curve *b* decreased monotonically and approached a constant value at a depth > 950 nm. For curve *c*, hardness rapidly decreased at a depth < 60 nm, and then increased within 60 nm to 230 nm to obtain the maximum value of 16.5 GPa. Curves *b* and *c* varied from curve *a*, indicating the presence of softer MPs in the film, which resulted in a rapid decrease in hardness at the outset. Therefore, the MPs involved in curves *b* and *c* corresponded to types 2 and 3, as presented in Fig. 8. For curve *d*, the hardness rapidly decreased at a depth < 50 nm and more slowly thereafter. At a depth > 400 nm, curve *d* exhibited an extremely slow increase in hardness, indicating that some MPs corresponding to type 4 in Fig. 8 existed in the film. The MPs corresponding to *b*, *c*, and *d* were also discussed previously [5].

3.6 Adhesion strength

The Rockwell indentation and scratch test are common methods of estimating the adhesion strength of films to substrates [36, 37]. Fig. 15 presents the microscopy

images of indentation tests at 150 kg for AlTiN films with various negative bias voltages. During the indentation test, the relevant information included the distribution and size of cracks around the indentation. When the load reached or went over the critical load, the shearing force was equal to or greater than the interfacial shear strength between the films and substrates. Thus, the partial removal of AlTiN films from the substrates occurred [37]. As shown in Fig. 15, the film deposited at -70 V was partially removed from the substrates. Only some cracks propagated around the indentation edge in the films deposited at -150 and -250 V, indicating that the films possessed better adhesion strength. The adhesion strength (HF) values were also given in Fig. 15.

The scratch test is generally accepted as one of the simplest methods of assessing the adhesion strength of films to the substrates. Three relevant parameters were proposed, namely, Lc1, Lc2, and Lc3, to interpret the adhesion. Lc1 denoted the critical load at which the first micro-cracking or cohesive damage occurred. Based on the definition, Lc1 represented the crack initiation load, hence, it can be considered the crack initiation resistance. The higher the Lc1, the more difficult initiating a crack in the film will be [38]. Lc2, at which an adhesive failure of the film occurred, was taken as a measure of film adhesion strength. Lc3 denoted the critical load at which films were completely peeled off from the substrates. Figs. 16 and 17 present the scratch adhesion profiles and the critical load of the films deposited at various negative bias voltages. The film deposited at -150 V achieved Lc1 and Lc2 values as high as 42 and 77 N, respectively. The lower adhesion obtained for the film deposited at -70 V was due to the lower bias applied to the samples, which produced the low energy that ad-atoms needed to migrate after arriving at the film surfaces. During deposition at -150 V, the ad-atoms obtained sufficient kinetic energy to migrate; thus, they exhibited better adhesion strength. The slight decrease in the adhesion strength of the film deposited at -250 V may be due to the overlarge bias voltage that led to a larger internal stress during film deposition.

3.7 Tribological properties of the films

The dependence of the friction coefficients for the AlTiN films under 20 N is presented in Fig. 18. The curves with various bias voltages showed different trends. The film deposited at -150 V exhibited a stable coefficient of friction (0.23) throughout the friction experiment. With an increase in voltage to -250 V, the coefficient of friction rapidly increased to 0.34 within the first 60 s, then slowly decreased to 0.25 and approached 0.22 after running for 1100 s. The coefficient of friction of the film deposited at -70 V rapidly increased to 0.3 at the initial stage but ceased afterwards because of the film damage caused by the high load and poor film adhesion. The initial coefficient of friction of the film deposited at -250 V was larger than that of the film deposited at -150 V, possibly due to the difference in hardness between the films deposited at -250 and -150 V bias voltages with counter-materials (WC-Co). Based on the results, the film deposited at -250 V exhibited a higher hardness value of 45 GPa, and the force required to deform and fracture the asperities on the film surface mainly contributed to the friction force during the initial friction stage [39].

4. Conclusions

In this study, AlTiN films were prepared by MAIP. The influences of negative bias voltage on the composition, deposition efficiency, microstructure, and mechanical properties of the MAIP AlTiN films were systematically investigated. Both the Al content and the deposition rate decreased with increasing negative bias voltage. The decrease in Al content was the hybrid effect of resputtering and CSD. The MPs on the film surfaces decreased with increasing negative bias voltage. The filtration mechanism was also discussed in terms of the ion bombardment mechanism and electrical repulsion theory. The XPS results revealed that the AlTiN films were composed of Ti-N and Al-N bonds. The hardness of the films increased with increasing negative bias voltage, with the film deposited at -250 V exhibiting the maximum hardness of 45 GPa. The types of MPs and their influence on the process of measuring hardness were also discussed. The adhesion and tribological tests showed

that the films deposited at -250 V showed the highest cracking resistance, the best adhesion ($L_c=78$ N and HF1), and the lowest stable coefficient of friction (0.23).

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Figure Captions:

Fig. 1 Effects of negative bias voltage on compositional contents: (a) Al, (b) Ti, (c) N, and (d) Al/(Al+Ti)

Fig. 2 Effects of negative bias voltage on the deposition rate of Al-Ti-N films

Fig. 3 XP spectra of AlTiN films deposited at (a)-70 V and (b) -150 V

Fig. 4 XRD patterns of Al-Ti-N films deposited at various negative bias voltages

Fig. 5 FE-SEM cross sections of Al-Ti-N films deposited at (a) -150 V and (b) -250 V

Fig. 6 Typical SEM image of AlTiN film deposited at (a) -150 V, (b) EDS of MPs, and (c) AlTiN film

Fig. 7 OM micrographs of Al-Ti-N films deposited at (a) -70 V, (b) -150 V, and (c) -250 V

Fig. 8 Schematic diagram of different types of MPs

Fig. 9 Particle density of Al-Ti-N films deposited at various negative bias voltages

Fig. 10 Load-displacement curves for films under various negative bias voltages

Fig. 11 Hardness vs. displacement for films deposited at various negative bias voltages

Fig. 12 Hardness values and elastic moduli of Al-Ti-N films deposited at various negative bias voltages

Fig. 13 Load-displacement curves for films with different types of MPs

Fig. 14 Hardness vs. displacement curves (a) for films with (b) different types of MPs

Fig. 15 Microscopy images obtained during the indentation test under 150 kg

Fig. 16 Scratch adhesion profile of the film deposited at (a) -70 V and (b) -150 V

Fig. 17 Critical load of AlTiN films deposited at various negative bias voltages

Fig. 18 Dependence of the friction coefficients for Al-Ti-N films under 20 N

Figure.1

Figure.2

Fig. 2

Figure.3

Figure.4

Figure.5

Figure.6

Figure.7

Figure.8

Fig. 9

Fig. 10

Fig. 11

Fig. 12

Fig. 13

Figure.14

Figure.15

-70 V

HF-5

-150 V

HF-1

-250 V

HF-2

Fig. 17

Fig. 18