Effect of pulsed bias on the properties of ZrN/TiZrN films deposited by a cathodic vacuum arc*

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ZrN/TiZrN multilayers are deposited by using the cathodic vacuum arc method with different substrate bias (from 0 to −800 V), using Ti and Zr plasma flows in residual N_2 atmosphere, combined with ion bombardment of sample surfaces. The effect of pulsed bias on the structure and properties of films is investigated. Microstructure of the coating is analyzed by X-ray diffraction (XRD), and scanning electron microscopy (SEM). In addition, nanohardness, Young's modulus, and scratch tests are performed. The experimental results show that the films exhibit a nanoscale multilayer structure consisting of TiZrN and ZrN phases. Solid solutions are formed for component TiZrN films. The dominant preferred orientation of TiZrN films is (111) and (220). At a pulsed bias of −200 V, the nanohardness and the adhesion strength of the ZrN/TiZrN multilayer reach a maximum of 38 GPa, and 78 N, respectively. The ZrN/TiZrN multilayer demonstrates an enhanced nanohardness compared with binary TiN and ZrN films deposited under equivalent conditions.

Keywords: physical vapor deposition, TiZrN films, pulsed bias, cathodic vacuum arc

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1. Introduction

Transition metal nitride is a protective film capable of improving the properties of the substrate material. The 4th group transition metal TiN has been commercially utilized for cutting and for mechanical tools. In addition, ZrN has attracted much attention for its good corrosion resistance, low resistivity,[1,2] better mechanical properties,[3,4] and more desirable golden color than TiN film.[5] Compared with conventional metal nitrides, ternary nitrides such as TiAlN, TiCrN, and TiZrN possess great advantages in microhardness and oxidation resistance due to their respective alloying effects. TiZrN films show an enhanced hardness compared with the binary TiN and ZrN films deposited under equivalent conditions.[6] This increased hardness shown by TiZrN films is due to a solid solution strengthening mechanism. Moreover, early studies on the effects of zirconium implantation on TiN coatings have shown improved wear resistance.[7,8] However, single layer films are still not sufficiently hard for practical use. Alternatively, multilayer thin films made of different phases have recently drawn a great deal of attention because the tool lifetime can be significantly increased, as compared to its single-layer counterpart.[9,10]

Many of the multilayer films reported in literatures are deposited by physical vapor deposition (PVD) techniques. In addition to PVD, the cathodic vacuum arc is particularly notable because it provides several advantages, such as high deposition rate, low processing temperature, as well as the ability to obtain a dense structure with stoichiometric composition. Although much research has been carried out on the ternary TiZrN films deposited by using the cathodic arc technique, information about the texture and properties of multilayer ZrN/TiZrN films changing with deposition parameters is limited. Substrate bias is a very important parameter for the deposition. A negative potential applied to the substrate is known to affect the structure, composition, and properties of TiAlN films significantly.[11] Ding *et al.*[12] found that the increase in substrate bias from −200 to −1000 V leads to an enhancement of the internal stress in TiC film. A recent development in the field of substrate bias is the application of pulsed bias at the substrate. A 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 compared with conventional DC bias.[13] Fessmann *et al.*[14] 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.

In this paper, the ZrN/TiZrN films are deposited by using the cathodic vacuum arc technique. Influences of pulsed bias voltage on microstructure, phase evolution, nanohardness, and adhesion strength are investigated.

2. Experimental process

ZrN/TiZrN films are deposited on silicon wafers and steel substrates by using the cathodic vacuum arc technique (as shown in Fig. 1) in N_2/Ar gas mixtures, using two separate

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face-to-face targets. The rotatable substrate holder is placed in the center of the chamber. The plasma is generated from the cathode spot on Ti and Zr targets (chamber wall used as anode). The arc current for target is 60 A and 80 A, respectively. High-speed steel (HSS), stainless steel, and silicon wafers with square of 10 mm × 15 mm are used as substrates.

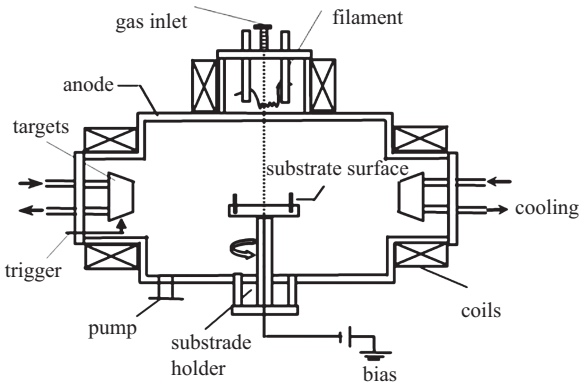


Fig. 1. Schematic diagram of the deposition device.

After being dried, they are put into the chamber with the polished surface parallel to the target surface. The specimens are cleaned ultrasonically in acetone and then in de-ionized water. Prior to deposition, the chamber is evacuated to a base pressure of 9×10^{-3} Pa, and then Ar^+ ions are introduced into the chamber to clean the substrates by sputtering. Before deposition, ion bombardment is carried out at a substrate bias voltage of -1000 V. Subsequently, the chamber is evacuated to reach 9×10^{-3} Pa again. During the deposition of films, nitrogen and argon gases are introduced into the deposition chamber, and the total pressure is kept constant at 0.8 Pa. The frequency and duty circle of the pulse bias are 50 kHz and 50:50, respectively. As the interlayer, a 100-nm-thick Zr layer is deposited between the substrate and the film. The process parameters are summarized in Table 1.

Table 1. Conditions for Ti–Al–N deposition process.

Compound target	Ti, Zr
Arc current/A	Ti: 60, Zr: 80
Total gas pressure/Pa	0.8
N_2 partial pressure (P_{n2}/P_t)	90%
Clearing time/min	60
Ion bombardment (interlayer)	-800 V, 5 min
Deposition time/min	Zr: 5, ZrN: 15, TiZrN: 30
Voltage of bias/V	$-50 \sim -800$
Duty cycle of bias	0.5
Frequency of bias/kHz	50

The microstructure, morphology, and thickness of the films are 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 (EDS), operated at voltage of 20 kV. Meanwhile, the deposition rate can be obtained by dividing the thickness with deposition time. The phase composition and crystal structure of the as-deposited films are identified by XRD (D/Max-2400) using Cu Kα radiation under conditions of 40 kV and 120 mA in θ–2θ geometry. The nanoindentation tests were performed using a nanoindenter II with a Berkovich indenter tip. The instrument is operated in the continuous stiffness node and the indentations are made by a constant nominal strain rate of 0.05 s^{-1}. The hardness and Young's modulus are determined using the Oliver analysis.[15] Three indentations are made for each film. The film adhesion is measured by an MFT-4000 scratch tester, the maximum load is 100 N, and the scratch distance is 5 mm. In this paper, a friction & wear tester (MS-T3000) is used to measure the coefficient of friction at room temperature. The ball material is Si_3N_4, the load was 1 N, and rotational rate was 400 rpm.

3. Results and discussion

The surface morphologies of ZrN/TiZrN multilayer films at different pulsed bias are shown in Fig. 2. A major concern for ZrN/TiZrN multilayer films deposited by the cathodic arc technique is the macroparticle formation.[16] It can be identified that the number and size of the macroparticles decrease markedly with the increase in the pulsed bias voltage.

The following two mechanisms are believed to dominate the effect of pulsed bias voltage on the macroparticles. The first is the ion bombardment mechanism.[17] At low bias voltages, the macro-particles are negatively charged because of low ionization within the macro-particles and the pick-up of electrons from the plasma.[18] The arc-evaporated Ti and Zr are ionized partially, the formation of TiZrN is insufficient, and large Ti and Zr droplets are not able to be ionized totally. These droplets deposit on the surface of substrate after random motion from the plasma, and hence macroparticles are formed. However, after bias voltage is applied, the arc plasma is accelerated by the external electric field. The collision between the incident ions and the growing coating occurs, which results in the removal of loosely bonded macroparticles. At higher bias voltage, the accelerated particles have higher momentum and more macroparticles are removed. Due to this bombardment effect, a honeycomb-like surface morphology is observed (see Figs. 2(e) and 2(f)), which agrees with the observation in another article.[19] The second effect is the electrical repulsion force at the near-substrate plasma sheath.[20] Huang *et al*. have systematically analyzed the model and explained the reduction mechanism of macroparticles in the pulsed bias process.[21] Before arriving at the surface of a substrate or a deposited coating, the macroparticles will collide randomly with electrons, ions, or neutral atoms absorbing them. These

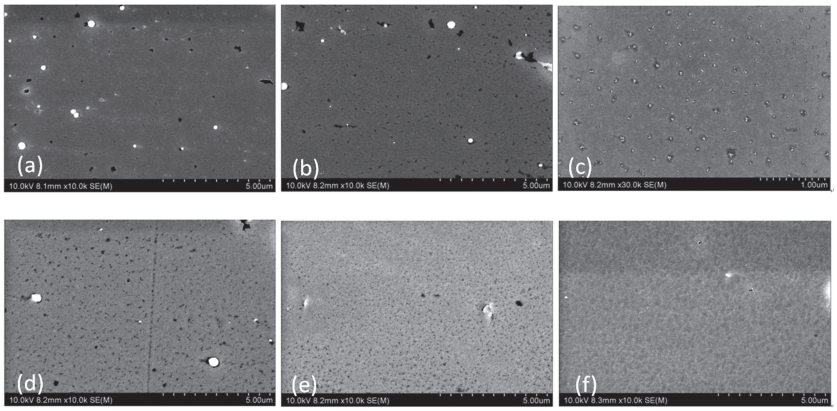


Fig. 2. Surface morphologies of ZrN/TiZrN multilayer films at different bias: (a) −5 V, (b) −10 V, (c) −200 V, (d) −300 V, (e) −500 V, and (f) −800 V.

collisions change the charging state of the macroparticles. Due to the large mass difference between electrons and ions, the charging effect from electrons is much stronger than that from ions, so a net negative charge happens on the surface of macroparticles.[22–24] Consequently, the negatively biased substrate can offer a repulsive force to the coming macroparticles, and result in the reduction of the macroparticles, higher bias voltage, stronger repulsive effect on the macroparticles, inducing smaller and fewer macroparticles being observed on the surface.

The variations of deposition rate with different pulsed bias are shown in Fig. 3. It can be seen that deposition rate decreases at first, then keeps almost constant until the substrate bias is up to −500 V. With a further increase in the substrate bias, the deposition rate decreases dramatically to 10 nm/min.

There are two main factors that affect the deposition rate. One is the accumulation effect, namely, the adhering of the particles which evaporate from targets to substrate. The other is the resputtering effect on the films, i.e., the flaking off the deposited films. The two factors compete with each other during the deposition process. At low bias voltage, the movement of the particles becomes directional towards the substrate. More particles are directed to the substrate. Although the particles' energy becomes larger, the accumulation effect is still dominant. Thus, the deposition rate decreases a little. With a further increase in the bias voltage, the resputtering effect is enhanced and hence the deposition rate decreases. In addition, the electrical repulsion mentioned above can also influence the changing tendency of the deposition rate. As a result, the deposition rate is decreased dramatically at high voltage.

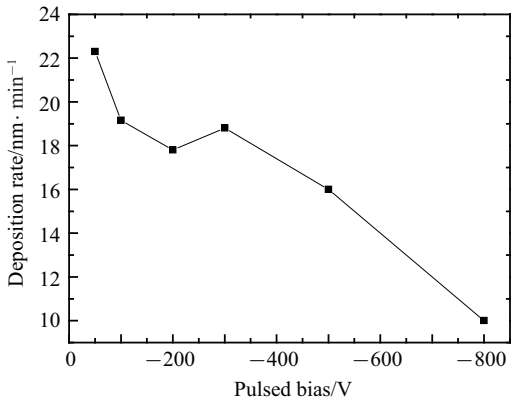


Fig. 3. Deposititon rate versus substrate bias.

Figure 4 shows the cross-section SEM images of the ZrN/TiZrN multilayer films at different bias. A columnar structure is observed in the cross-sectional films with low bias

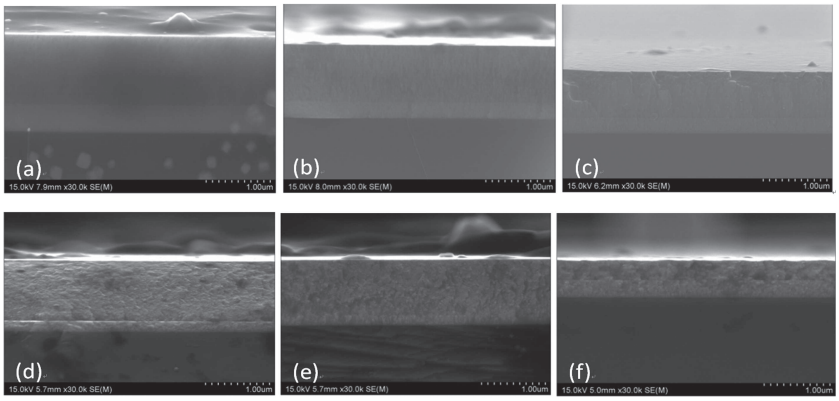


Fig. 4. Cross-section SEM image of ZrN/TiZrN multilayer films at different bias: (a) −5 V, (b) −10 V, (c) −200 V, (d) −300 V, (e) −500 V, and (f) −800 V.

voltage (see Figs. 4(a)–4(c)), while the cross-sectional films deposited with high bias voltage (see Figs. 4(d)–4(f)) show more homogeneous and denser images. The grains of the films change from columnar to equiaxial structure. All these indicate that the dense films require a high deposition bias voltage, i.e., high ion energy. It can be concluded that the bombardment or impingement of energetic ions resulted in a compaction effect on the films. In case that the ion energy is not high enough, diffusion in surface layers takes place as the ions cannot penetrate into the interior structure. The incoming ions will be trapped on the growing surface and tend to generate cross-linked structure, which results in a loose and rough surface. If the energy exceeds the critical value for atomic displacement in the structure, the ions can penetrate deeply into the interior of the structure. Then the ion energy tends to be dissipated into the volume nearby. Consequently, dense and smooth films are formed when the bias voltage increases to a proper value.

Bias voltages show significant effects on the preferred orientation and crystallinity of TiZrN films, as shown in Fig. 5. The XRD spectra indicate a strong tendency of forming the TiZrN (111) texture at low bias voltage. With the bias increasing up to −300 V, the (111) peak becomes distorted and splits. Peak broadening at higher bias voltage is evident. This indicates that a multi-phase structure is formed, i.e., binary TiN and ZrN, and ternary TiZrN phases may simultaneously appear in the films. The possible reason is that the distribution of Ti and Zr ions from one target to another is not homogeneous. Further increase in the substrate bias leads to the formation of (220) preferred orientation. Both (111) and (220) peaks are diminished as the bias voltage is increased to more than −300 V. At all investigated substrate bias voltages, the films have a columnar structure (see Fig. 4), similar to that of binary ZrN films and the same preferred orientation. A similar texture changes with the bias voltage was observed for TiZrN films by Uglov.[25]

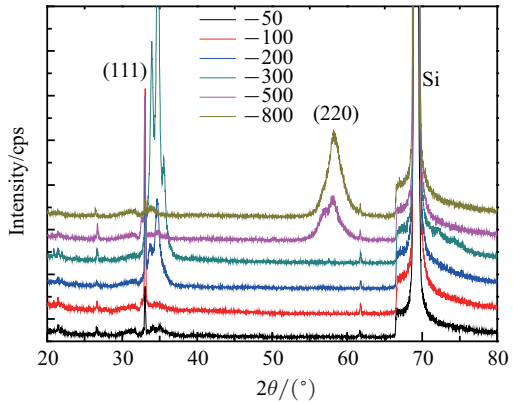


Fig. 5. (color online) XRD patterns of TiZrN films at different bias.

The nanohardness and Young's modulus of ZrN/TiZrN deposited with various bias voltages are presented in Fig. 6. The nanohardness of ZrN and TiN films deposited under the same condition is also shown. The texture evolutions of ZrN, TiN, and ZrN/TiZrN show similar tendencies.

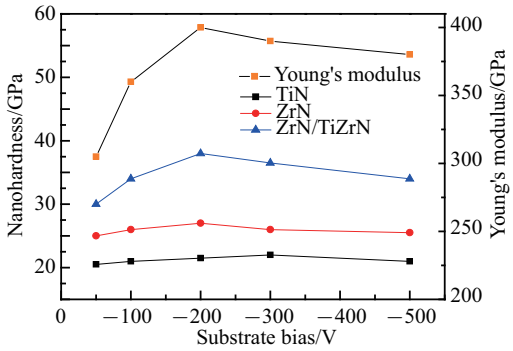


Fig. 6. (color online) Nanohardness and Young's modulus of the films as functions of the bias voltages.

Compared with that of binary films, the nanohardness value of ZrN/TiZrN films is significantly higher. This may be ascribed to a solid-solution strengthening mechanism. Increase in the bias voltage leads to the enhancement of the pack density and (111) preferred orientation, which results in the increase in the nanohardness. The highest hardness value is close to 38 GPa. With a further increase in the bias voltage, the hardness decreases. This is attributed to the formation of a (220) texture and more defects at higher bias. With the increase in the bias voltage, a stronger bombardment effect, which leads to higher temperature, should be taken into account.

Figure 7 reveals that the adhesion strength varies with the substrate bias. The scratch critical load (L_c) of the films increases from 60 to 75 N with the increase of substrate bias from −50 to −100 V, and then the L_c changes slightly with the increase in bias to −500 V. With further increasing substrate bias up to −800 V, the L_c drops to 45 N. The pack density, bombardment, and implantation effect are enhanced with the increase in the substrate bias, which results in the improvement of adhesion strength. Meanwhile, the residual stress is also enhanced, which can probably lead to the decrease in the adhesion strength.

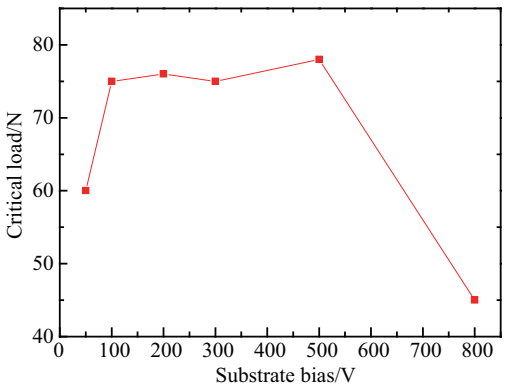


Fig. 7. (color online) Scratch critical load of ZrN/TiZrN films with different substrate bias.

4. Conclusion

ZrN/TiZrN multilayer films are produced using a cathodic vacuum arc process with a pulsed substrate bias. The separate Ti and Zr targets are used to produce plasma flows. The film is composed of TiN, ZrN, and TiZrN ternary phases. At low pulsed bias, the films exhibit a columnar microstructure with preferred (111) orientation. With the increase in bias voltage, the preferred orientation of film changes from (111) to (220). The cross-section SEM images show that a dense and homogeneous multilayer structure is formed. With the increase in the bias voltage, the number of macroparticles is greatly eliminated by the ion bombardment mechanism and electrical repulsion force from near substrate plasma sheath. The nanohardness and L_c approach the highest values of about 38 GPa and 78 N, respectively. The ideal mechanical properties of the films are obtained at a bias of -200 V.

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