Effects of bias on surface properties of TiN films fabricated by hollow cathode discharge

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Titanium nitride (TiN) films have been deposited on AISI 304 stainless steel substrates using hollow cathode reactive plasma vapor deposition. Titanium is introduced by sputtering the Ti cathode nozzle and TiN is formed in the presence of a nitrogen plasma excited by radio frequency. The substrate bias voltage is varied from 0 to −300 V to investigate its effect on the mechanical and structural properties of the films. X-ray diffraction results show the formation of TiN (111) and Ti2N (220) phases in the films. The sample bias has a critical influence on the thickness of the deposited films. The bias of −200 V leads to the thickest films (about 1680 nm) and the deposition rate is 18.7 nm/min. The microhardness, root-mean-square (rms) roughness values, and tribological properties also exhibit nonlinear relationship with increasing bias voltages. The highest hardness of about 1027 hardness vickers and best wear resistance are achieved at a bias voltage of −100 V. Atomic force microscopy results reveal the lowest rms surface roughness of 3.19 nm when the bias voltage is −200 V. © 2007 American Vacuum Society. [DOI: 10.1116/1.2748803]

I. INTRODUCTION

Owing to its superior mechanical properties, titanium nitride (TiN) films are widely utilized in many industrial areas where high abrasion resistance, low friction coefficient, high-temperature stability, and high hardness are required.1 The technologies of preparing TiN films are generally divided into physical vapor deposition (PVD) and chemical vapor deposition (CVD).2 PVD has gained more interest due to low-temperature processes compared to CVD.3

The TiN films fabricated by PVD has a long history and earlier reports may go back to 1977.4,5 Some of the previous studies have focused on the relationship between the mechanical properties and the parameters of deposition. For instance, the adhesion at the coating/substrate interface and the hardness of films can be optimized by varying the flow of reactive gas during deposition.6 The hardness of TiN films decreases with increasing bias, and also decreases with increasing nitrogen pressure in a hollow cathode discharge ion plating system.7 In filtered arc evaporation, the substrate bias may be varied to control the energy of the bombarding ions which in turn affects the hardness, stress, adhesion, roughness, crystal orientation, and grain size.2 Pihosh et al.8 reported that the tribological properties of the deposited TiN films strongly depend on the total pressure of N2/Ar reactive gas mixture in a magnetron sputtering system. The mechanical properties of TiN are strongly related to its preferred orientation,9 and TiN films with (111) preferred orientation possess the highest hardness.10,11 The residual stress is also a significant factor influencing the preferred orientation and hardness of the coating.12

In this study, TiN films are fabricated on AISI 304 stainless steel substrate by a special approach (e.g., radio frequency hollow cathode reactive physical vapor deposition). A radio frequency hollow cathode discharge source has a small size and can deliver a high local plasma density. Therefore it is more suitable for plasma processing of the selected surface of the components. This work focuses on the characterization of TiN coatings with varying bias and the effects of the bias voltage on the surface roughness, film thickness, phases, hardness, and frictional properties of the TiN films are investigated.
II. EXPERIMENTAL DETAILS

A schematic diagram of the radio frequency (rf) hollow cathode plasma jet (RHCPJ) is depicted in Fig. 1. The cylindrical hollow cathode Ti nozzle (6 mm in outer diameter, 2 mm in inner diameter, and 25 mm in length) was connected to the rf generator. Cooling water was circulated to control the temperature of the cathode nozzle and avoid overheating of the cathode. The cathode nozzle was fabricated from a 99.99% pure titanium rod. The substrates were AISI 304 stainless steel 20 mm in diameter and 5 mm in thickness. The samples were affixed on the substrate holder and oriented perpendicular to the hollow cathode nozzle which was 30 mm away. Before loading into the vacuum chamber, the samples were polished by diamond paste with size of 1 μm and cleaned in an ultrasonic bath using acetone and alcohol for 10 min. The purity of Ar and N₂ gases used in our experiments was 99.99% and the base pressure before deposition was $7 \times 10^{-3}$ Pa.

Prior to deposition of the TiN films, the samples were sputter cleaned by Ar ions for 10 min at a pressure of 1.2 Pa, bias voltage of −4 kV, and rf power of 400 W. Subsequently, a Ti interlayer was first deposited by hollow cathode self-erosion using Ar gas pressure of 6.5 Pa and rf power of 450 W. The rf reflected power was relatively low due to better matching, so it was not taken into account. The bias was applied to the substrate by a separate pulse power supply with frequency of 10 kHz and pulse width of 20 μs. After 30 min, deposition of TiN was initiated by introducing a mixture of Ar [20 SCCM (SCCM denotes cubic centimeter per minute at STP)] and N₂ (4.5 sccm) to the pressure of 7 Pa into the vacuum chamber. The sample bias was varied from 0 to −300 V for different sets of specimens. The deposition processes lasted for 90 min and the rf power was kept at 350 W.

The surface morphology and rms roughness of the TiN coatings were determined using atomic force microscopy (AFM). The thickness of the TiN coatings was calculated using cross-sectional scanning electron microscopy (SEM) micrographs and the structural phases were determined by x-ray diffraction (XRD). Dry sliding tests were carried out with a ball-on-disk tribometer under laboratory atmosphere (room temperature of 25 °C; relative humidity ranging from 30% to 40%). A load of 150 g was applied to a GCr15 ball 6.35 mm in diameter. The hardness of the TiN coatings was evaluated by a Vickers microhardness tester under a load of 25 g and the loading time was 10 s. Three measurements were taken to yield statistical averages.

III. RESULTS

The thicknesses of the TiN films fabricated at different biases are shown in Fig. 2. The sample bias has an evident influence on the deposition rate of the TiN films. The film thicknesses increase with increasing substrate biases from 0 to −200 V but decrease when the bias voltages continue to increase. The estimated deposition rates of TiN film fabricated at 0, −100, −200, and −300 V biases are 12.8, 13.9, 18.7, and 16.7 nm/min, respectively. Figure 3 shows the cross-sectional SEM image of the sample deposited at −200 V. The TiN film appears dark and the stainless steel substrate is brighter.

Figure 4 shows the surface micrographs of the samples deposited at 0, −100, −200, and −300 V, respectively. The surfaces show salient islandlike structures that become

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**Fig. 1.** Schematic diagram of the radio frequency hollow cathode plasma jet.

**Fig. 2.** Thicknesses of TiN films fabricated at different biases.

**Fig. 3.** Cross-sectional SEM images of the sample prepared at −200 V.
smaller and smoother as the substrate bias changes from 0 to −200 V. However, further increase (i.e., −300 V) leads to a slightly different surface. Figure 5 shows the rms roughness of the different samples measured by AFM. The rms roughness values decrease sharply from 8.198 nm (0 V) to about 3.190 nm (−200 V) and then increase to a high value of 6.031 nm at −300 V bias.

Figure 6 shows the x-ray diffraction spectra acquired from the TiN thin films deposited at substrate biases of 0, −100, −200, and −300 V.
−200, and −300 V, respectively. TiN (111) and Ti$_2$N (220) have been detected but the main peak TiN (200) is not observed. The intensities of TiN (111) and Ti$_2$N (220) change with sample biases. The intensity of TiN (111) becomes larger and Ti$_2$N (220) becomes lower when the bias voltage changes from 0 to −300 V.

The hardness values of TiN films deposited at different biases are displayed in Fig. 7. The TiN film produced at −100 V has the highest hardness value [hardness vickers (HV) 1027], and the enhancement in hardness is approximately 280% in comparison with that of the AISI 304 stainless steel substrate (HV 267). Lower or higher sample biases appear to adversely affect the surface hardness. The tribological properties of the TiN coatings are studied using ball-on-disk measurements at atmospheric pressure. Figure 8 shows the plots of the friction coefficients and electrical signals as a function of number of cycles at a load of 150 g and sliding speed of 23.6 mm/s. The electrical signals are employed to evaluate the breakthrough of the films. All the TiN films show low friction coefficients of 0.5 before breakthrough. The electrical signals are fairly constant before breakthrough, which is indicated by a sharp decrease. Figure 9 shows the number of breakthrough cycles for different samples. Consistent with the hardness measurements, the sample deposited at −100 V shows the largest breakthrough cycle of about 4800. For comparison, the average electrical signals of the different samples before breakthrough are also shown in Fig. 10. Here, the sample deposited at −100 V has the lowest value of electrical signal and lower or higher sample biases lead to higher electrical signals.

![Figure 7](image7.png)  
**Fig. 7.** Variation of microhardness values of TiN films with substrate biases.

![Figure 8](image8.png)  
**Fig. 8.** Plots of friction coefficients and electrical signal vs number of cycles for TiN film fabricated using different biases: (a) 0 V, (b) −100 V, (c) −200 V, and (d) −300 V.

![Figure 9](image9.png)  
**Fig. 9.** Number of cycles before breakthrough determined from sample fabricated at different bias samples.
that the films have a (111) preferred orientation regardless of the substrate bias voltage (Fig. 6). This phenomenon is commonly observed in TiN films deposited by physical vapor deposition.\textsuperscript{17} The observed (111) preferred orientation may be attributed to the minimization of strain energy due to the fact that this plane has the lowest strain energy in face centered cubic materials.\textsuperscript{18} In our experiments, the Ti$_2$N (220) peak is also observed at lower or no bias but only TiN (111) appears at higher biases, as shown in Fig. 6. Hence, the energy effects here may be somewhat different. With increasing bias voltages, the ion energy becomes higher and a larger volume of the substrate/film materials is affected per incident ion due to deeper ion penetration. The number of defects may increase due to ion bombardment, resulting in recrystallization and consequently facilitating the formation of an orientation that is favorable on the denser (111) type.\textsuperscript{8}

Our results illustrate that there is an optimal bias for the best surface hardness. The Vickers hardness values increase as the biases increase from 0 to −100 V and then decrease as the bias voltages increase further. Park \textit{et al.}\textsuperscript{19} have observed similar results in TiN films prepared by sputter ion plating using bias voltages from 0 to −300 V. It is well known that the measured hardness of a hard coating on a soft substrate is influenced by several factors such as preferred orientation,\textsuperscript{20} film thickness,\textsuperscript{21} crystalline size,\textsuperscript{22,23} and residual stress.\textsuperscript{24} The sample prepared at −100 V possesses the highest hardness which may be attributed to the formation of duplex TiN and Ti$_2$N phases. It has indeed been reported that the film composed of TiN and Ti$_2$N has higher hardness compared to a single-phase film composed of TiN.\textsuperscript{25} In fact it may also be related to the internal stress generated by bombardment of highly energetic ions.\textsuperscript{26,27} It has been reported that the enhancement of the hardness in thin films is affected by a high compressive stress.\textsuperscript{28,29} Therefore a proper stress may be needed to achieve higher hardness, otherwise the material may undergo plastic flow and a reduction in stress in the film if the energy of incident ions is too high.\textsuperscript{30} Compared to sample prepared at zero bias, the samples deposited using a sample bias have higher hardness. A smaller grain size increases grain boundaries and dislocations, consequently leading to an increased hardness.\textsuperscript{31} Chou\textsuperscript{11} has reported that the thickness of the TiN coating is very important from the perspective of hardness. The measured hardness may increase with thicker films.\textsuperscript{32} In addition, a previous study on single crystal films shows that (111) is the hardest orientation of TiN due to the geometrical factor on the slip system.\textsuperscript{33} Therefore, if the film has a highly (111) preferred orientation, it should have higher hardness.\textsuperscript{34}

Figure 8 shows the friction coefficients in dry sliding tests conducted between the ball and the TiN films. The various samples do not show significant differences in the friction coefficients before breakthrough. The electrical signals passing through the films are recorded to investigate the tribological behavior. An abrupt change in the electrical signal indicates breakthrough of the TiN films and exposure of the AISI 304 steel substrate. The films thickness and phase structure are two important factors governing when breakthrough
occurs in the TiN films. In our experiments, although the TiN film produced at −100 V has a lower thickness compared to those fabricated at −200 and −300 V, it possesses excellent tribological properties as manifested by breakthrough occurring after 4800 cycles (Fig. 9). It may be due to the existence of the Ti,N (220) phase that has higher wear resistance than TiN. In contrast, the sample treated at zero bias has the smallest film thickness of 1150 nm and the weakest TiN tribological properties as manifested by breakthrough occurs in the TiN films. In our experiments, although the TiN properties.

−100 V has the lowest electrical signal and best tribological voltages. It is probably due to the variation of the film structure, thickness, density, and so on. The sample prepared at −100 V has the lowest electrical signal and best tribological properties.

V. CONCLUSION

TiN films are deposited on AISI 304 stainless steel substrates using hollow cathode reactive physical vapor deposition. The substrate bias is observed to have a significant effect on the surface topography, coating thickness, hardness, and tribological properties of the deposited TiN films. Our experimental results demonstrate an optimal bias for the best surface properties. The film deposited at −200 V shows the lowest surface roughness and largest thickness. The sample fabricated at −100 V has the highest surface hardness and excellent tribological properties attributable to the dual TiN and Ti,N phases.

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