The study of composition, structure, mechanical properties and platelet adhesion of Ti–O/TiN gradient films prepared by metal plasma immersion ion implantation and deposition

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Abstract

Titanium oxide and titanium nitrogen gradient films were prepared by three different processes using metal plasma immersion ion implantation and deposition (MPIII-D). The mechanical properties of the films synthesized on silicon wafers, Ti6Al4V and low temperature isotropic carbon (LTIC) were evaluated by nano-indentation, pin-on-disc wear, and scratching test. The hardness of the film was measured to be 19.5 GPa. Investigation by XRD shows that the surface Ti–O layer possesses a rutile structure and analysis by X-ray photoelectron spectra (XPS) discloses that the surface composition of the synthesized TiN/Ti–O films is non-stoichiometric. The gradient characteristics of the films were corroborated by qualitative analysis of secondary ion mass spectroscopy (SIMS). The thickness of films was 510–940 nm. Platelet adhesion experiments adopted to estimate the blood compatibility of the films show that the adsorption and deformation of platelets on the synthesized TiN/Ti–O gradient films have been significantly suppressed compared to LTIC. Scanning electron microscopy (SEM) used to assess the wear and scratch tracks discloses that the films exhibit good wear resistance and high adhesion strength.

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1. Introduction

Titanium nitride is commonly used as hard and corrosion resistant coatings in cutting tools, machines, and also biomaterials due to its superior mechanical and chemical properties such as high hardness, good abrasion proof and chemical stability [1]. In the past decade, many researchers have investigated the blood compatibility of titanium oxide films and reported that titanium oxide films possessed good blood compatibility [2,3]. Huang et al. [4,5] have prepared rutile type titanium oxide ceramics layers utilizing ion beam assisted deposition (IBAD), and the films exhibit more superior
blood compatibility than widely accepted clinical biomaterials such as LTIC. Hence, TiN/Ti–O compound films have large potential as biomaterials since it combines the advantages of titanium nitride and titanium oxide. Several methods have been used to synthesize TiN/Ti–O gradient films, such as DC sputtering, ion beam enhanced deposition (IBED), plasma-based ion implantation (PBII), and plasma immersion ion implantation (PIII) [6–9]. Since the 1990s, PIII has received much attention in the field of ion beam surface modification and many new applications have emerged. PIII circumvents the line-of-sight restriction plaguing traditional beam-line ion implantation, eliminates complex focusing elements in the instrument, is capable of processing complex-shaped components such as artificial organs, and is potentially more economical [9,10]. In this work described in this paper, TiN/Ti–O films were synthesized by metal plasma immersion ion implantation and deposition (MPIII-D) on Si(1 0 0), Ti6Al4V and LTIC substrates. The mechanical properties and blood platelet adhesion were studied.

2. Experimental

The schematic diagram of PIII device is shown in Fig. 1. Ti ions were created from a Ti cathodic arc source and diffused into the vacuum chamber via a magnetic duct to reduce deleterious macro-particles, and a negative bias voltage applied to the target accelerated the Ti plasma towards into the target. A nitrogen or oxygen gas plasma was simultaneously established in the vacuum chamber sustained by an external radio frequency plasma source [11]. The Ti and gas ions are introduced into the target to form the gradient films on Si(1 0 0), Ti6Al4V and LTIC substrates. Before the samples were put on the target holder, they were cleaned by acetone, alcohol and deionized water. Prior to deposition, the samples were sputtered for 10 min by Ar ions to remove surface contamination. The experimental parameters and sample numbers are shown in Table 1. During deposition, the gas flow ranged from 1.5 to 99.5 sccm, as shown in Fig. 2. It can be seen that the main difference between T1 and T2 lies in the transition from N2 to O2. The transition in the former case was linear, whereas the latter one was abrupt. Hence, the TiN and Ti–O interfaces in samples T1 and T2 are different. In order to study the film adhesion strength, the two samples were subject to scratch tests and the results will be discussed later in this paper.

The structure and composition of the synthesized films were determined by X-ray diffraction (XRD) employing the Al kα (1486.6 eV) line and

Fig. 1. Schematic diagram of PIII-D device.
40 kV–40 mA power, X-ray photoelectron spectra (XPS) and secondary ion mass spectrometry (SIMS). The wear tests were performed on a pin-on-disk wear tester employing a 6 mm diameter Si$_3$N$_4$ ball. Nano-indentation was used to assess the hardness of the gradient films on Si, and a maximum hardness of 19.5 GPa was obtained.

Adhesion of the gradient film on LTIC was evaluated by a WS-97 scratch test apparatus produced by Lanzhou Chemistry & Physics Institute (China). The morphology of the films after the wear and scratch tests were monitored by scanning electron microscopy (SEM), and the wear theory was applied to explain the results.

Blood adhesion experiments were conducted in a class 10,000 cleanroom. The samples were distributed evenly in two culture dishes. 200 ml blood extracted from a healthy adult was centrifuged to form the blood-rich plasma (PRP) and erythrocyte, and then blood was injected into the culture dishes. After culturing at 37 °C for 20 min and 2 h respectively, the samples were fixed for one hour using 2% glutaraldehyde and 12 h using 5% glutaraldehyde. Finally, the morphology of the adherent platelets were investigated by SEM after critical desiccation [12].

3. Composition and structure

The X-ray diffraction patterns acquired from samples T1 and T3 on Si substrate are displayed in Fig. 3. The gradient films on T1 is composed of primarily rutile TiO$_2$(110), anatase TiO$_2$(204) and TiN(111), but no obvious peaks can be observed in T3 except the Si peak. During deposition, when the metal ions, gas ions as well as metal-gas molecular ions impinge into the sample, heat is generated and the substrate temperature is elevated thereby benefiting nucleation. However, because a high frequency bias voltage is not applied to T3, Ti ions are only accelerated to a low velocity, and the substrate temperature is thus lower. It fact, our temperature measurement after

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Process</th>
<th>Bias voltage</th>
<th>Time (min)</th>
<th>Metal parameters</th>
<th>Sputtering parameters</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>Fig. 1(a)</td>
<td>2000 V</td>
<td>70</td>
<td>Magnetic field current: 10 A; average current of basic arc: 8–9 A; frequency: 60 Hz; pulse width: 1 ms</td>
<td>RF power: 500 W; bias voltage: ~1 KV; time: 10 min</td>
<td>Base pressure: 5.6 × 10$^{-4}$ Pa; work pressure: 5.0 × 10$^{-2}$ Pa</td>
</tr>
<tr>
<td>T2</td>
<td>Fig. 1(b)</td>
<td>+50 VDC</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T3</td>
<td>Fig. 1(a)</td>
<td>50 VDC</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>
deposition indicates that the average temperature of T1 is about 100 °C higher than that of T3. Moreover, a high frequency bias voltage enhances bonding between the Ti and O ions, and consequently, compared to T3, T1 exhibits better crystal formation and T3 essentially shows non-crystalline properties.

Fig. 4 shows the XPS spectra acquired from T1 on Si after the surface has been sputter cleaned by argon ions. Figs. 4(a) and (b) illustrate the typical deconvolution of the Ti2p and O1s XPS peaks using Gaussian–Lorentzian fitting (80% Gaussian and 20% Lorentzian) and by approximating the contribution of background by the Shirley method. The peak positions at 464.51, 462.65 and 459.76 eV shown in Fig. 4(a) correspond to the core levels of Ti4+ 2p1/2, Ti3+ 2p1/2 and Ti2+ 2p1/2, respectively, whereas the 458.94, 458.08 and 456.49 eV peaks can be attributed to Ti4+ 2p3/2, Ti3+ 2p3/2 and Ti2+ 2p3/2. Oxygen is observed to exist only in one chemical state due to the presence of only one peak at 529.9 eV as shown in Fig. 4(b). The oxygen is intrinsic to the film and not adsorbed because the sample is pre-sputtered prior to the XPS measurement (about 10 nm of materials are sputtered off). The high resolution XPS scans acquired from titanium oxide indicates that the valence state of Ti consists of Ti4+, Ti3+ and Ti2+. The synthesized Ti–O film is obviously non-stoichiometric and TiO2, Ti2O3 and TiO can be identified. The atomic Ti to O ratios in TiO2, Ti2O3 and TiO are 0.5, 0.67 and 1.0, respectively. The surface Ti and O concentrations in the synthesized gradient films can be calculated from the respective fitted peak areas (Fig. 4) divided by archival atomic sensitivity factors [13] (1.20 for Ti and 0.66 for O). The calculated result of Ti to O is about 0.66 further corroborating the presence of TiO, Ti2O3 and TiO2.

Fig. 5 depicts the SIMS data. After taking into account diffusion effects, the thickness of the films is estimated to be around 940, 750 and 510 nm to T1–T3 from Figs. 5(a) and (c). The gradient characteristic of the films is shown by Figs. 4 and 5. The interface between TiN and Ti–O is located at 230–320 nm. The Ti profile in T3 shows a second peak around 480 nm in Fig. 5(b), and it is situated at the interface between TiN and Ti–O shown in Fig. 5(a). The abnormal peak may originate from some signal interference of impurities absorbed in the TiN and Ti–O interface and perhaps matrix effects.

4. Mechanical properties

4.1. Nano-indentation testing

The nano-hardness of the as-deposited films was determined using a high resolution nano-mechanical test instrument produced by CSEM Corporation. A Berkovich 90° diamond tip with a radius of ~20 nm was used. The test employed a partial unloading load function that maintained a 1-mN/min loading and unloading rate. The projected contact area, A, was determined from a tip-shape polynomial function of the contact depth at maximum indentation load. The reduced elastic modulus is given by $E_r = \left(1 - \nu_s^2\right)/E_i + \left(1 - \nu_t^2\right)/E_t$, where $E_i$, $E_t$, $\nu_t$ and $\nu_s$ are the elastic moduli and Poisson’s ratio of the indenter and the substrate materials, respectively. For a diamond indenter, $E_i$ is 1140 GPa and $\nu_t$ is 0.07 [14]. The reduced elastic modulus is calculated from the force-indentation depth curve based on the relationship $E_r = S/2(\pi/A_t)^{1/2}$ where $S$ is the elastic stiffness as slope of the indentation curve at the beginning of unloading (dP/dh). The unloading stiffness ($S$)
is calculated by fitting the unloading curve to the power law relation $P = A(h - h_i)^m$, where $A$, $h$, and $m$ are arbitrary fitting parameters. The stiffness can be calculated from the derivative of the equation $S = \frac{dP}{dh(h_{\text{max}})} = mA(h_{\text{max}} - h_i)^{m-1}$. The hardness is defined by the ratio of the maximum load to the projected contact area, $H = \frac{P_{\text{max}}}{A}$. The contact area is determined from a tip calibration.
function $A(h_c)$ where $h_c$, the contact depth, is derived using the following equation: $h_c = h_{\text{max}} - \frac{\Delta P_{\text{max}}}{S}$, where $\varepsilon$ equals 0.75.

Fig. 6 exhibits the nano-indentation load versus displacement curves obtained from T1, T2 and T3 on Si substrate. It can be seen that the displacement for sample T1 is the smallest among the three samples. The slope is approximately constant for sample T1 and T2 from 0 to 0.5 mN, implying that the two samples are both in the elastic deformation regime. On the other hand, the slope for sample T3 changes from 0 to 0.5 mN and the change occurs at around 0.3 mN where a small flat region is manifested, and it explains that the film may have defects when the diamond indenter penetrates to this depth. The slope of sample T1 and T2 is greater than that of T3, meaning that sample T1 and T2 have a higher Young's modulus and hardness. From the load-displacement curves obtained from the nano-indentation test, the nano-hardness of the samples can be calculated. The nano-hardness of samples T1, T2 and T3 are 19.5, 17.5 and 8.28 GPa, respectively. The nano-hardness results show that a high frequency bias voltage contributes to increased hardness.

4.2. Wearing testing

The wear properties of T1, T2 and T3 on Ti and LTIC substrates were investigated by a pin-on disk test using a 6 mm diameter $\text{Si}_3\text{N}_4$ ball, 4 mm wearing radius, and 50 g load. The friction coefficient as a function of cycles after 15,000 revolutions is shown in Fig. 7. It can be seen that the wear resistance of T1 relative to T2 and T3 is increased significantly. In the entire test period, the friction coefficient of T1 on Ti6Al4V substrate is much lower than that of T2 and T3. Moreover, prior to 14,000 revolutions, the variation of the friction coefficients of T1 on LTIC substrate is the same as that of Ti6Al4V, although opposite results...
emerge after 14,000 revolutions. It is believed that the film is continuously rubbed off during our test and the Si$_3$N$_4$ ball comes into direct contract with the LTIC substrate. As a result, graphite powders are gradually produced reducing the friction coefficient decreased slowly. During our test, the friction coefficient of T1 always exhibits a low value, compared to T2 and T3. It can be inferred from Figs. 6 and 7 that a voltage of 2 kV yields the best improvement in wear and hardness. Moreover, the existence of the change in the slop contributes to the improvement in wear as illustrated by the results acquired from T1 and T2.

4.3. Adhesion testing

The film adhesion was assessed using a WS-97 scratch test instrument. The diamond indenter moves linearly along the samples at a constant speed and continuously increasing force. When the diamond indenter to which a piezoelectric transducer is connected penetrates a certain depth, the films begin to break thereby producing acoustic signals that are captured by the piezoelectric transducer. The signals are then amplified by a preamplifier and output to indicate film adhesion. The morphology of the wear and scratch tracks were monitored by SEM and the results are depicted in Fig. 9. Fig. 9(a) displays the morphology of the wear track. The film surface exhibits abrading and fatigue wear, whereas the coating does not delaminate after 15,000 revolutions with the exception of sporadic puncturing at a few points thereby showing that the coating is quite hard and has good wear resistance. The edges of the wear track are ragged and deformation slip bands are visible indicating plastic deformation of the materials close to the tracks. The morphology of tip of the scratch track is shown in Fig. 9(b). During the scratch process, coating cracking and delamination are not due to force exerted to the coating. Only plastic deformation can be observed, and so film adhesion appears to be quite strong. Furthermore, the inner stress and thermal expansion
Fig. 8. Scratch test results illustrating adhesion of synthesized films: (a) T1 on Ti6Al4V substrate, (b) T1 on LTIC substrate, (c) T2 on Ti6Al4V substrate and (d) T2 on LTIC substrate.

Fig. 9. SEM micrographs of wear and scratch tracks: (a) Ti6Al4V (×500) and (b) tip of the scratch tracks on LTIC (×1000).
coefficient of the gradient coatings are relaxed and accordingly, the anti-cracking ability of the film is enhanced. On the other hand, for a single coating, crack can more easily occur during the wear test, and coupled with the effects of the inner stress of the film-substrate, film detachment results. Therefore, our gradient coatings yield better properties than to a single coating [17].

5. Platelet adhesion experiment and discussion

LTIC is generally regarded to be an acceptable anticoagulant material and thus chosen here as a control for comparison. Platelet adhesion experiments that characterize the degree of blood compatibility were performed on our gradient films and control. The adhered platelet morphology is shown in Fig. 10. Fig. 10(a) shows the LTIC surface. It can be seen that platelet adhesion is quite substantial and some of the platelets have aggregated showing stretched pseudopods. The results indicate that platelet activation is quite serious on LTIC. Fig. 10(b) illustrates the results on our TiN/Ti–O gradient films. Accumulation of platelets is greatly reduced here, and only a few platelets germinate pseudopods. The majority of the platelets remain unactivated. Our results thus unambiguously illustrate that TiN/Ti–O gradient films are superior to LTIC with regard to blood compatibility. Previous studies have shown that blood undergo a series of changes when it comes in contact with a foreign surface materials. Adhesion followed by conformational change in the plasma protein [18] activates the platelets resulting in thrombus formation. Our experiments demonstrate that the scalar and active level of adhesion platelets on the TiN/Ti–O gradient films are much lower than those on LTIC. Thus, TiN/Ti–O gradient materials are potential substitute for LTIC as anticoagulant materials.

6. Conclusion

Titanium oxide and titanium nitride gradient films were prepared by three different processes using metal plasma immersion ion implantation and deposition (MPIII-D) on Si(100), Ti6Al4V and LTIC substrates. The hardness of the gradient film is better than that of a single film and the nano-hardness of the gradient film can be as high as 19.5 GPa. The gradient coating also exhibits good wear resistance and adhesion. A high bias voltage is one of the main factors improving the abrasion resistance and adhesion. The existence of the graded layer in the gradient coatings is also believed to account for the improvement in the wear and film adhesion properties. According to our platelet adhesion results, the synthesized TiN/Ti–O gradient film has better anticoagulation

Fig. 10. Platelet adhesion morphology (×3000): (a) LTIC and (b) TiN/Ti–O gradient film of T1 on Si substrate.
properties compared to LTIC. Hence, TiN/Ti–O
gradient materials are a potential substitute to
LTIC in blood contacting applications.

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References

Appl. 8 (1994) 404.
Cai, Z.H. Zhen, F. Zhang, Y.R. Chen, X.H. Liu, T.F. Xi,
[9] Y.X. Leng, P. Yang, J.Y. Chen, H. Sun, J. Wang, G.J.
Instr. 68 (4) (1997) 1866.
[12] P. Yang, N. Huang, et al., Chinese J. Biomater. Eng. 21
1564.
[18] H.Q. Gu, Biomedical Materials, Tian Jin, China: Published