Structure and properties of biomedical TiO₂ films synthesized by dual plasma deposition

Y.X. Leng¹, N. Huang¹, P. Yang²,³, J.Y. Chen²,³, H. Sun¹, J. Wang¹, G.J. Wan², X.B. Tian³
R.K.Y. Fu³, L.P. Wang³, P.K. Chu*²

¹Department of Materials Engineering, Southwest Jiaotong University, Chengdu, PR China
²Department of Physics & Materials Science, City University of Hong Kong, 83 Tai Chee Avenue, Kowloon, Hong Kong, PR China

Abstract

Titanium metal and titanium alloys are among the most widely used materials in biomedical devices because of their relatively high corrosion resistance and good biocompatibility. It has been suggested that the physicochemical and dielectric properties of the surface native oxide play a crucial role in the biocompatibility. There is increasing evidence that titanium may be extensively released in vivo and, under certain conditions, accumulated in adjacent tissues or transported to distant organs. Therefore, it is necessary to synthesize thicker and denser TiO₂ films on titanium to enhance its biomedical properties. In this paper, we discuss our fabrication technique utilizing dual plasma generated by metal vacuum arc and radio frequency. The films fabricated consist of rutile crystal, although the substrates are not heated. As the oxygen partial pressure is raised, the intensity of the (101) and (110) diffraction peaks increases, and that of the (002) diffraction peak decreases. The preferred orientation of the TiO₂ film shifts from (002) to (110) as a result of the competition between the surface free energy and ion bombardment. At low oxygen pressure, the TiO₂ grain growth is mainly affected by ion bombardment, whereas thermodynamic factors affect the film growth at higher oxygen partial pressure. When the oxygen partial pressure reaches 0.93 × 10⁻¹⁰ Pa, further increase in the oxygen flow rate does not change the film composition. The film is completely oxidized and only comprises the TiO₂ phase. The microhardness of the TiO₂ films increases with the oxygen partial pressure and reaches a maximum value of 19 GPa at 1.7 × 10⁻¹³ Pa. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Titanium oxide; Microstructure; Microhardness; Metal vacuum arc plasma source; Surface morphology

1. Introduction

Titanium oxide is widely used in optical and electrical applications because of its high refractive index and dielectric constant. It is also very attractive as a biocompatible protective coating on medical implants, where a protective surface layer of TiO₂ considerably increases the wear resistance and hardness. The dissolution of Ti metal ions from rutile is one order of magnitude lower than that from anatase, so that rutile is the preferred phase with respect to biomedical applications [1]. Several techniques to prepare titanium dioxide films have been reported, such as thermal oxidation [1], anodic oxidation [2], magnetron sputtering [3–6], cathodic vacuum arc deposition [7–9], plasma immersion implantation (PIII) [10,11] and ion beam-enhanced deposition (IBED) [12]. PIII circumvents the line-of-sight restriction inherent to conventional beam-line ion implantation and eliminates complex focusing elements in the instrument. It is thus capable of processing large and complex-shaped components and is potentially more economical and efficient than many competing techniques [13–15]. In this paper, a dual plasma deposition technique derived from PIII to synthesize titanium oxide thin films for biomedical applications is discussed.

2. Experimental

The plasma-immersion ion implantation system used in this work is schematically shown in Fig. 1. It is equipped with several plasma-generating tools, including radio frequency (RF) discharge, hot-filament discharge and a vacuum arc metal plasma source [16]. A Ti cathode, 14 mm in diameter, was mounted on the metal
vacuum-arc plasma source. An oxygen plasma was sustained by RF in the vacuum chamber and, at the same time, a titanium plasma was generated in the metal arc source and diffused into the vacuum chamber via a magnetic duct to eliminate deleterious macro-particles. The Ti–O films were deposited as a function of oxygen gas pressure. The voltage on the sample was \(-50 \text{ V DC}\) and the deposition time was 60 min. The deposition rate varied from 0.1 to 0.15 nm/s, depending on the oxygen gas flow. In order to increase adhesion between the film and silicon (100) substrate, a \(-3 \text{kV}\) pulse voltage (10 kHz, 5 \(\mu\)s) was applied to the sample during the first 10 min. Table 1 lists the instrumental parameters. The films were subsequently annealed in situ at 700 \(^\circ\)C for 60 min and then at 750 \(^\circ\)C for 30 min at a base pressure of \(1.5 \times 10^{-3} \text{ Pa}\). The annealing apparatus comprised a resistively heated quartz tube.

The crystalline structure of the films was measured using X-ray diffraction (XRD) with a CuK\(_\alpha\) source. The microhardness of the films was determined employing a HXD100-B microhardness tester using a load of 50 mN. In order to minimize substrate effects on the film hardness and measure the true hardness of the film, the nano-hardness and elastic modulus of sample \#2 were measured with a CSEM nano-hardness tester equipped with a diamond indenter and an equilateral base (Ber-kovich indenter). The maximum load was 0.5 mN and the loading rate was 1 mN/min. The adhesion strength between the substrate and film was assessed using the CSEM nano-scratch tester. The initial load was 0.1 mN, final load was 50 mN and the load rate was 49.9 mN/min.

### 3. Results and discussion

As shown in Fig. 2, the structure of the films is rutile crystal, although the substrates were not heated. This is different from the amorphous TiO\(_2\) materials synthesized by magnetron sputtering \([3,5]\). It is believed that the phase transformation in the case of dual-plasma deposition is dominated by the high energy and concentration of the incident ions. Ti ions have an initial kinetic energy of approximately 50 eV when they are generated in the metal vacuum-arc plasma source. After they diffuse into the vacuum chamber via the magnetic duct, they are further accelerated by a \(-50 \text{-V}\) bias, and thus the total energy is over 100 eV, depending on the charge state of the ions. According to the diagram of Lölbel et al. \([17]\), the substrate temperature and energy of the particles impinging into the substrate are relevant parameters affecting the film microstructure. Fig. 2 also illustrates that, at low oxygen partial pressure, such as \(0.63 \times 10^{-2} \text{ Pa}\), the main phase is Ti\(_2\)O. When the oxygen partial pressure reaches \(0.93 \times 10^{-2} \text{ Pa}\), only rutile TiO\(_2\) exists in the films, as indicated by the dominant (002) peak. This suggests that the crystallites preferentially grow on the (002) plane parallel to the surface. As the oxygen partial pressure increases, the

<table>
<thead>
<tr>
<th>Table 1 Instrumental parameters for samples #1–5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen gas flow (sccm)</td>
</tr>
<tr>
<td>#1</td>
</tr>
<tr>
<td>#2</td>
</tr>
<tr>
<td>#3</td>
</tr>
<tr>
<td>#4</td>
</tr>
<tr>
<td>#5</td>
</tr>
<tr>
<td>Oxygen partial pressure ((\times 10^{-2}) Pa)</td>
</tr>
<tr>
<td>#1</td>
</tr>
<tr>
<td>#2</td>
</tr>
<tr>
<td>#3</td>
</tr>
<tr>
<td>#4</td>
</tr>
<tr>
<td>#5</td>
</tr>
<tr>
<td>RF power (W)</td>
</tr>
<tr>
<td>#1</td>
</tr>
<tr>
<td>#2</td>
</tr>
<tr>
<td>#3</td>
</tr>
<tr>
<td>#4</td>
</tr>
<tr>
<td>#5</td>
</tr>
</tbody>
</table>

Vacuum arc metal plasma source for all samples: pulse repetition rate, 65 Hz; pulse width, 1 ms; and arc current, 180 A.
intensity of the (101) and (110) diffraction peaks increases, while that of the (002) diffraction peak diminishes. It can thus be concluded that growth on the (110) plane parallel to the surface becomes more dominant at higher oxygen partial pressure.

If a film is prepared in the absence of ion beam bombardment, such as by evaporation or sputtering, the preferred orientation is often determined by thermodynamic parameters. In general, the crystal plane with the lowest Gibbs free energy will grow preferentially. That is to say, the preferred orientation is the one having the lowest surface free energy. When ion bombardment is utilized during film growth, the preferred orientation can be altered. The preferred orientation change of TiO₂ from (002) to (110) is a result of the competition between the surface free energy and ion bombardment. At low oxygen partial pressure, the mean free path of Ti ions is long and the energy loss due to collisions in the plasma is small. Hence, the TiO₂ grain growth is mainly affected by the energy deposited by the incoming ions. At higher oxygen partial pressure, the Ti ion mean free path is shorter and energy loss due to collisions in the plasma is higher. The average energy of the Ti ions is therefore smaller when they reach substrate. At the
same time, a higher oxygen plasma density leads to a larger number of implanted oxygen ions and more substantial heating of the substrate. At higher temperature, the diffusion coefficients of the atoms in the films are larger, and thus the film growth is affected more by thermodynamic factors. In order to confirm our postulation, TiO$_2$ films were synthesized at different substrate temperature, and also using an oxygen atmosphere but without triggering the plasma (to isolate out the effects of ion bombardment). Fig. 3 shows the XRD spectra of these samples. The first sample, ‘a’, was synthesized in a neutral oxygen atmosphere, that is, no RF discharge, and the preferred orientation of the TiO$_2$ film is observed to be (002), i.e. the plane with a higher Gibbs free energy. Due to the absence of significant heating from oxygen ions, the substrate temperature in this experiment was lower than 50°C. At this temperature, atomic diffusion is not significant and the preferred orientation is mainly affected by ion bombardment. Sample ‘b’ in Fig. 3 was also deposited under a neutral oxygen atmosphere, but at a higher substrate temperature of 400°C. The preferred orientation is (110), which has the lowest Gibbs free energy. At this higher temperature, atomic diffusion is more significant and the preferred orientation is influenced more by thermodynamic factors. When an oxygen plasma was sustained using RF at 600 W (sample ‘c’ in Fig. 3), oxygen ions bombard the substrate, heating it to approximately 100°C. The atoms in the films diffuse more easily and thus thermodynamic factors and ion bombardment both play a role in the film growth. Therefore, the (110) plane with the lowest Gibbs free energy and the (002) plane favored by ion bombardment coexist.

Fig. 2 shows that the full width at half-maximum (FWHM) of the peaks is broad, which is indicative of a small grain size. Fig. 4 displays the morphology of samples #3 and #3a (sample #3 annealed in vacuum in situ) acquired by contact-mode atomic force micros-
copy (AFM). The films are quite dense and do not show gross voids. Sample #3 is composed of grains 50–80 nm in size, whereas sample #3a has larger grains exceeding 400 nm.

Fig. 5a shows the Ti 2p X-ray photoelectron (XPS) peak acquired from the surface of sample #3. The top surface consists solely of TiO, with no evidence of Ti$_2$O$_3$ and TiO suboxides. The binding energies of the Ti 2p$^{1/2}$ and Ti 2p$^{3/2}$ peaks are 461.4 and 466.9 eV, respectively, assigned to Ti$^{4+}$ in TiO$_2$ with a peak separation of 5.5 eV. It should be noted that, since titanium and titanium suboxides are easily oxidized in air to form TiO$_2$, the XPS spectrum may not convey the complete story. Therefore, argon ion sputtering was used to clean the sample surface before acquiring a second set of XPS spectra. Fig. 5b,c shows the results and fitting of the Ti 2p$^{1/2}$ and Ti 2p$^{3/2}$ peaks acquired from samples #2 and #3 after 4 min of argon sputtering. In addition to Ti$^{4+}$, other peaks corresponding to 459.58 and 465.18 eV can be deconvoluted. These two peaks are due to Ti$^{3+}$ in Ti$_2$O$_3$. The Ti$^{3+}$ signal emerges from ion sputtering of TiO$_2$, preferentially depleting the film of oxygen [18], and it can be inferred that both films have been fully oxidized to TiO$_2$. This also means that after the oxygen partial pressure reaches 0.93 x 10$^{-2}$ Pa, further increasing the oxygen flow has a small effect on the film composition because the films have been fully oxidized.

Fig. 6 displays the microhardness data acquired from samples #1–5. The microhardness values increase with oxygen partial pressure up to 1.7 x 10$^{-2}$ Pa, at which the maximum microhardness of 19 GPa is attained. However, further increase in the oxygen pressure degrades the microhardness. It is well known that the microstructure of the films affects the hardness of the film. Increasing the oxygen partial pressure causes structural modification (preferred orientation) that is responsible for changes in the hardness [19]. We are...
investigating this behavior in more detail and will report our results later.

Because the TiO$_2$ films fabricated in our experiments are not very thick (<1 μm), the hardness measured can be affected by the substrate. In order to measure the microhardness of the film more accurately, the nano-hardness and Young’s modulus of sample #2 were measured using a CSEM nano-hardness tester. The hardness measured reaches 1979 HV and the Young’s modulus is 152.6 GPa. In addition, almost all coatings applications require strong film adhesion. The adhesion modulus is 152.6 GPa. In addition, almost all coating hardness measured reaches 1979 HV and the Young’s modulus of sample #2 was measured using the CSEM nano-scratch tester. The first cracking load was 22 mN. Sample #2 was studied using SEM, and the micrograph shows that the film crack is a result of film atom link abating. As no flaking is observed, the film adhesion is quite strong.

4. Conclusion

Titanium oxide thin films were synthesized by titanium and oxygen dual-plasma deposition. The films are dense and do not exhibit gross voids. The films consist of rutile crystal, although the substrates were not heated, contrary to the amorphous films deposited using magnetron sputtering. As the oxygen partial pressure is increased, the intensity of the (002) and (110) diffraction peaks increases, while that of the (002) diffraction peak decreases. The preferred orientation changes from (002) to (110) as a result of the competition between the surface free energy and ion bombardment. At low oxygen pressure, the TiO$_2$ grain growth is mainly affected by ion bombardment, but at higher oxygen pressure, the film growth is more affected by thermodynamics. When the oxygen partial pressure reaches 0.93×10$^{-2}$ Pa, further increase in the oxygen flow rate does not have an appreciable effect on the film composition, since the film has already been fully oxidized. The microhardness of the TiO$_2$ films achieves a maximum value of 19 GPa at 1.7×10$^{-2}$ Pa, and the film adhesion strength is adequate.

Acknowledgments

The work described in this paper was jointly supported by Chinese NSFC 39870199, Key Basic Research #G1999064706, High Tech Project 102-12-09-1, Hong Kong Research Grants Council (CERG #9040498 or CityU 1032/00E), and City University of Hong Kong (SRG #7001177).

References