Influence of oxygen pressure on the properties and biocompatibility of titanium oxide fabricated by metal plasma ion implantation and deposition

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Abstract

Titanium oxide with a rutile structure has superior optical properties and blood compatibility and is thermodynamically more stable than other forms. Titanium oxide thin films are deposited on (1 0 0) silicon and SiO₂ wafers by metal plasma ion implantation and deposition. The substrates are DC biased during the film deposition and the influence of the oxygen pressure on the characteristics of the coatings is investigated. X-ray diffraction indicates the existence of TiO in the film when the oxygen pressure is lower than 2.0 × 10⁻² Pa. As the oxygen pressure increases, the preferred orientation of the as-deposited titanium oxide film changes to the (2 0 0) high-index plane from the (1 0 0) low-index plane. The as-deposited titanium oxide films are subsequently annealed at 750 °C for 60 min in vacuum. The microstructure, resistance, composition, and blood compatibility of the films are assessed. Before annealing, the sheet resistance of the titanium oxide increases with higher oxygen pressure, and after vacuum annealing, the sheet resistance of some of the titanium oxide films increases by approximately 60 times. The results of the platelet adhesion experiments acquired from the annealed samples are similar to those from low-temperature isotropic pyrolytic carbon.

Keywords: Titanium oxide; Metal plasma ion implantation and deposition; Microstructure; Sheet resistance; Composition

1. Introduction

Titanium oxide is one of the most important materials in the optical, electronic, and chemical fields and a recent application is its use as a biocompatible protective coating on medical implants [1]. Rutile type titanium oxide ceramics and thermally oxidized TiO₂ and TiO₂₋₋, prepared by ion beam assisted deposition generally have good blood compatibility, especially oxide layers with thickness exceeding 40 nm [1–5]. TiO₂ is known to crystallize in three different crystallographic structures: rutile (tetragonal), anatase (tetragonal), and brookite (orthorhombic). The rutile form is the most compact and stable and has been most widely used. Titanium oxide thin films can be fabricated by various methods such as radio frequency (RF) sputtering [6–8], filtered arc deposition [9,10], metal–organic chemical vapor deposition [11], plasma immersion ion implantation (PIII) [12–14], plasma enhanced CVD [15,16], thermal spray [17], plasma spray [18], anodic oxidation [19], and ion beam enhanced deposition techniques [4].

A metal cathodic arc with a low-voltage and high-current plasma discharge takes place in vacuum. The cathodic arc process is an ideal method for assisted film deposition, since the cathode spot is an intense source of ionized material with energies sufficient for self-densification when condensing onto a substrate surface. The ion fraction from the arc source can be as high as 100%. In this study, TiO₂ films are deposited onto (1 0 0) silicon and SiO₂ substrates using metal plasma ion implantation and deposition (PIII-D) and the effects of the oxygen pressure on the film characteristics are evaluated. The relationship between the film characteristics and blood compatibility is also studied.
2. Experimental

Titanium oxide thin films were deposited onto heated Si (1 0 0) and SiO₂ wafers by metal PII-D using an apparatus shown in Fig. 1. It was equipped with several plasma generating tools, including RF discharge, hot-filament discharge, and a vacuum arc metal plasma source [20]. A Ti cathode of 14 mm in diameter was mounted onto the metal vacuum arc plasma source. The 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 titanium oxide films were deposited as a function of oxygen gas pressure and the deposition conditions are listed in Table 1. In order to increase the adhesion between the film and substrate, a –3 kV pulse (10 kHz, 5 µs) was applied to the sample during the first 10 min. The films were subsequently annealed in situ at 750 °C for 60 min at a base pressure of 1.5 × 10⁻³ Pa. The microstructure of the films was measured using X-ray diffraction (XRD) with a Cu Kα source. The composition and the sheet resistance of the titanium oxide films were determined using X-ray photoelectron spectroscopy (XPS) and four-point probe measurements, respectively.

Platelet adhesion tests were performed on the titanium oxide and low-temperature isotropic pyrolytic carbon (LTIC) to compare their blood compatibility. The quantity and morphology of the adhered platelets were examined. Blood was first obtained from a healthy adult volunteer and was collected in an acid citrate dextrose medium. After centrifugation, red cells and platelets were speared and a platelet-rich plasma was obtained. The samples were immersed into the platelet-rich plasma and incubated at 37 °C for 20 min and 3 h, respectively. After rinsing, fixing, and drying at the critical point, the specimens were examined using scanning electron microscopy and optical microscopy. Twenty different locations were chosen at random to obtain a good statistical average.

3. Results and discussion

Fig. 2 shows the XRD patterns of the as-deposited films fabricated at different oxygen pressure P₂O₅. When P₂O₅ is lower than 0.83 × 10⁻² Pa, only the TiO₂ phase can be observed, but as the oxygen pressure increases, the Ti₃Oₓ phase becomes dominant. The results imply that the higher index planes grow preferentially parallel to the surface. When the oxygen pressure reaches 2.0 × 10⁻² Pa, only rutile TiO₂ exists in the films. As the oxygen pressure increases, the intensity of the (2 0 0) diffraction peaks goes up while that of the (1 1 0) diffraction peak diminishes, and I₂O₅(2 0 0)/I₂O₅(1 1 0) increases as shown in Fig. 3. It can thus be concluded that the (2 0 0) plane parallel to the surface becomes more dominant at higher oxygen pressure.

The substrate temperature and energy of the particles impinging into the substrate are important parameters affecting the film microstructure. If the temperature is prepared...
in the absence of ion beam bombardment such as evaporation or sputtering, the preferred orientation is often determined by thermodynamic constraints. 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 TiO from (110) to (200) is a result of the competition between the surface free energy and ion bombardment. At low oxygen pressure, the effect of oxygen bombardment alone is observed to be small. However, when the substrate temperature reaches 400 °C, the diffusion coefficients of the atoms are larger, and so the film growth is affected more by thermodynamic factors. The preferred orientation is (110) that has the lowest Gibbs free energy. Hence, the TiO grain growth on the (110) plane parallel to the surface becomes more dominant at lower oxygen pressure. At higher oxygen pressure, there are more oxygen ions bombarding the film, and more oxygen will condense onto the TiO film when the pulsed metal vacuum arc plasma source is off. As a result, more oxygen condenses onto the TiO film as the oxygen pressure increases and the TiO crystal lattice is strained to accommodate these extra oxygen atoms. In fact, the XPS results reveal that the ratio of O/Ti is bigger than 2 as the oxygen pressure reaches 2.3 × 10⁻² Pa. Therefore, at high oxygen pressure, growth along the (200) plane favored by ion bombard-

![Fig. 2. XRD patterns of the as-deposited titanium oxide films.](image)

![Fig. 3. Intensity ratios derived from XRD results.](image)

Fig. 4. XRD patterns of the annealed titanium oxide films (750 °C, 60 min).

ment and oxygen condensation becomes more dominant. However, when the oxygen pressure reaches 7.1×10⁻² Pa, the mean free path and oxygen ion energy decrease and consequently, the effect of ion bombardment diminishes. At the same time, thermodynamic constraints play a more important role, and so the $\frac{I_{TiO_x}(200)}{I_{TiO_x}(110)}$ ratio decreases as shown as in Fig. 3.

After the samples are annealed at approximately 750 °C for 1 h, the diffraction peaks become sharper as shown in Fig. 4. The grain size of the film is also bigger than that of the as-deposited film. The Ti2p XPS spectrum of the surface of the as-deposited film is typical of all as-deposited films. Only one 80% Gaussian–20% Lorentzian peak can be assigned to each peak of the Ti2p doublet ($2p_{1/2}$ and $2p_{3/2}$) indicating a single oxidation state of +4 characteristic of TiO₂ [21]. The top surface consists solely of TiO₂ with no evidence of Ti₂O₃ and Ti suboxides. It should be noted that since titanium and titanium suboxides are oxidized easily in air to form TiO₂, 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. High resolution Ti2p $2p_{1/2}$ and Ti2p $2p_{3/2}$ peaks were acquired from the as-deposited and annealed samples fabricated at an oxygen pressure was 2.0×10⁻² Pa after 4 min of argon sputtering. For the as-deposited sample, in addition to Ti, other peaks corresponding to 459.6 and 465.2 eV can be deconvoluted. These two peaks are due to Ti³⁺ in Ti₂O₃. After vacuum annealing, the Ti2p peak shows some differentes compared to the as-deposited film. No Ti³⁺ can be detected and so re-oxidation may occur in the 750 °C vacuum anneal.

The O/Ti atomic ratios calculated from the as-deposited films using the XPS data are displayed in Fig. 5. The O/Ti ratio of the sample deposited at an oxygen pressure of 2.3×10⁻² Pa is larger than the stoichiometric ratio of two for TiO₂. The deviation from the stoichiometric O/Ti ratio in XPS can be explained by the presence of species such as oxygen atoms adsorbed onto the film surface. The O1s peaks acquired from the as-deposited and annealed titanium oxide films after 4 min argon sputtering can be deconvoluted into three peaks at 530.8, 531.8 and 532.8 eV binding energies that can be attributed to O–Ti (O1), O–O (O2), O–H (O3). The relative weightings of O1 and (O2+O3) are listed in Table 2. The results indicate that the amount of adsorbed oxygen (O2+O3) diminishes after vacuum annealing and it may be due to evaporation and diffusion into the bulk.

The sheet resistance of the samples was measured and the results are shown in Fig. 6. In general, the sheet resistance of as-deposited samples increases with higher oxygen pressure. The sheet resistance of the as-deposited samples shows a sharp increase when the oxygen pressure exceeds 2.0×10⁻² Pa, as shown in Fig. 6. When the oxygen pressure is less than 2.0×10⁻² Pa, the O/Ti ratio is less than 2. Titanium suboxides and vacancies exist in the films and enhance electrical conduction. When the oxygen pressure is larger than 2.0×10⁻² Pa, the O/Ti ratio is larger than 2. There exists a superfluous amount of oxygen in the film and no suboxides can be found. Thus, the resistance increases sharply. After annealing, the crystal lattice defect decreases and the sheet resistance increases as shown in Fig. 6.

Adhered platelets are usually measured to assess hemocompatibility, and activation of platelets is a more important parameter indicating the interaction of blood with the materials than the adhesion behavior. In our experiments, the hemocompatibility of the stoichiometric titanium oxide was studied. Before annealing, there are some crystal defects in the films, and the hemocom-
Fig. 5. O/Ti atomic ratios of Ti–O films.

Table 2
Relative weightings of O1 and (O2+O3) in as-deposited and annealed samples

<table>
<thead>
<tr>
<th>Oxygen pressure (Pa)</th>
<th>As-deposited O1</th>
<th>(O2+O3)</th>
<th>Annealed O1</th>
<th>(O2+O3)</th>
</tr>
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<tr>
<td>0.83 × 10^{-2}</td>
<td>0.83</td>
<td>0.17</td>
<td>0.91</td>
<td>0.09</td>
</tr>
<tr>
<td>2.0 × 10^{-2}</td>
<td>0.70</td>
<td>0.3</td>
<td>0.73</td>
<td>0.27</td>
</tr>
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Fig. 6. Sheet resistance of the titanium oxide films.

Compatibility is much poorer than that of LTIC. After annealing, the crystal defects are reduced, and the films exhibit enhanced blood compatibility. Deformation of the adhered platelets on the titanium oxide surface is studied semi-quantitatively to evaluate the hemocompatibility [22], and the results are shown in Table 3.

The degree of deformation (pseudopodium) and aggregation of the adhered platelets on the annealed samples prepared at oxygen pressure of 3.4 × 10^{-2} and 5.1 × 10^{-2} Pa are similar with those of LTIC for an
incubation time of 20 min. For an incubation time of 180 min, the degree of deformation and aggregation is less than that on LTIC. Our data demonstrate that the blood compatibility of the samples produced at oxygen pressure of $3.4 \times 10^{-2}$ and $5.1 \times 10^{-2}$ Pa is as good as that of LTIC.

4. Conclusion

Titanium oxide thin films are synthesized by titanium metal vacuum arc plasma deposition. When the oxygen pressure reaches $2.0 \times 10^{-2}$ Pa and the substrates are heated to 400 °C, the films consist of rutile crystals. As the oxygen pressure increases, the intensity of the (2 0 0) diffraction peak increases while that of the (1 1 0) diffraction peak decreases. The preferred orientation changes from (1 1 0) to (2 0 0) 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 thermodynamics, but at higher oxygen pressure, the film growth is more affected by the TiO$_2$ crystal lattice distortion to accommodate more oxygen ion adsorbed onto the TiO$_2$ film. When the oxygen pressure is larger than $2.0 \times 10^{-2}$ Pa and the O/Ti ratio is larger than 2, no suboxides can be detected and so the extra amount of oxygen is absorbed or dissolved in the films. During annealing, the extra oxygen may react with Ti or out-diffuse to the vacuum. As the oxygen pressure increases, the sheet resistance of the as-deposited samples increases, and the sheet resistance of the as-deposited samples exhibit a sharp increase when the oxygen pressure exceeds $2.0 \times 10^{-2}$ Pa. After annealing, the crystal defects diminish, and the sheet resistance increases by about a factor of 60 in some samples. The blood compatibility of some of the samples is experimentally proven to be as good as that of LTIC.

Acknowledgments

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References


<table>
<thead>
<tr>
<th>Oxygen pressure (×10^{-2} Pa)</th>
<th>20 min</th>
<th>180 min</th>
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<tbody>
<tr>
<td>2.3</td>
<td>III&quot;</td>
<td>IV&quot;</td>
</tr>
<tr>
<td>3.4</td>
<td>II&quot;</td>
<td>III'</td>
</tr>
<tr>
<td>5.1</td>
<td>II''</td>
<td>III'</td>
</tr>
<tr>
<td>LTIC</td>
<td>II''</td>
<td>IV&quot;&quot;</td>
</tr>
</tbody>
</table>

The degree of deformation of the adhered platelets on the surface of the films can be categorized into four types [22]: I: There are adhered platelets on the surface of sample, but the platelets are not activated; I': number of adhered platelets is less, I'": more, I'"": much more. II: The adhered platelets are activated and begin to exhibit pseudopodium; II": a portion of platelets exhibit pseudopodium; II"": many platelets showing pseudopodium. III: Adhered platelets activated further and aggregated; III": a portion of platelets aggregated; III'": many platelets aggregated. IV: Aggregated platelets forming net structures with fibrin; IV": aggregated platelets net structure; IV"": erythrocytes adhered onto the net structure.