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Structure and Properties of Ti-O-N Films Synthesized by Reactive Magnetic Sputtering

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Abstract

Ti-O-N films with different structure and composition were synthesized on silicon wafer by reactive unbalanced magnetron sputtering at different X which represents the flux ratio of N₂/ (O₂+N₂). As X increases from 0% to 100%, the structure of the films changes from TiO₂ to TiN gradually. The crystal TiN is found only in the film fabricated in 100% N₂. The band gap and the sheet resistance of films decrease with X increasing. Surface energy and water contact angle of Ti-O-N films were not influenced by X. The blood compatibility of Ti-O-N films got worse with X increasing.

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Key word: Ti-O-N films; magnetic sputtering; blood compatibility; band gap;

1. Introduction

In the last decades, artificial heart valves had been almost made of low temperature isotropic pyrolytic carbon (LTIC). However, the blood compatibility of LTIC is not satisfied for long-term performance and the patients must continuously depend on the anti-coagulation medicine to prevent the formation of thrombus. The blood compatibility of titanium oxides films is better than traditional biomaterials such as stainless steel and LTIC [1-11]. Recent years some researches focused on Ti-O-N films and there are some reports about the investigation and application of Ti-O-N films in biomedical field [7,8,12]. The clotting time of Ti-O-N films deposited by metal plasma immersion ion implantation and deposition (MePIIID) was longer than pure rutile film [12]. However its adhesion and activation of platelets were worse than pure rutile. However, there is few work reported the blood compatibility of Ti-O-N film synthesized by magnetron sputtering method.

In this work, Ti-O-N films were fabricated on silicon wafer and glass substrate by reactive unbalanced magnetic sputtering. The film structure, composition, semiconductor properties, water contact angle, surface energy and blood

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compatibility were investigated. The relation between blood compatibility and its physical-chemical properties is discussed.

2. Experimental details

The depositions of Ti-O-N films were performed at different X which represents the flux ratio of N₂/(O₂+N₂) on UBMS450 magnetic sputtering system. The system includes a vacuum chamber, vacuum pump system, four sputtering targets and a sample holder. The background and the working gas pressure were 1.0×10⁻³ Pa and 0.4 Pa respectively. Before deposition, the samples and target were cleaned by argon ion bombardment for 6 and 3 minutes respectively. Experimental details are listed in Table 1.

<table>
<thead>
<tr>
<th>sample</th>
<th>TiON0</th>
<th>TiON0.5</th>
<th>TiON0.7</th>
<th>TiON0.82</th>
<th>TiON1</th>
</tr>
</thead>
<tbody>
<tr>
<td>X=N₂/(N₂+O₂)×100%</td>
<td>0</td>
<td>50%</td>
<td>70%</td>
<td>82%</td>
<td>100%</td>
</tr>
<tr>
<td>Sputtering current (A)</td>
<td>Direct current</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bias voltage (V)</td>
<td>Direct current</td>
<td>-50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>323</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar pressure(Pa)</td>
<td>0.26</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Target-substrate distance (mm)</td>
<td>180</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deposition time (min)</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The structure of Ti-O-N film was investigated by X-ray diffraction spectroscopy (XRD) in grazing incidence geometry (ω=0.7°) with a Philips X’Pert diffractometer (CuKα radiation). The film composition was investigated by X-ray photoelectron spectroscopy (XPS). The sheet resistance was determined by four-point probe sheet resistance measurement. The band gap of Ti-O-N films was obtained according to Tauc method assisted by using ultraviolet spectrophotometry. Sessile drop contact angle methods were used to determine the wettability and surface energy. Blood compatibility was characterized in terms of platelet adhesion and activation. The quantity and morphology of the adherent platelets were observed by SEM and optical microscope. Blood was provided by a healthy adult volunteer and was collection in an acid citrate dextrose medium. Platelet rich plasma was produced by low speed centrifugation of the blood. The samples were immersed into the platelet-rich plasma and incubated at 37°C for 2 hours. After rinsing, fixing, dehydration in alcohol and critical point drying, the samples were examined by scanning electron microscopy and optical microscopy. Twenty different locations were chosen randomly to obtain an objective statistical average [3].

3. Results and discussion

![Fig.1 Structures of Ti-O-N films](image-url)
The structure of the Ti-O-N films on silicon wafer was checked by XRD and the results indicate that it is affected by X value. As shown in Fig.1, at X=0 and X=50%, there are no obvious difference. Both TiON0 and TiON0.5 almost consist of anatase, as well as some rutile. At X=70%, the structure of TiON0.7 is different from TiON0 and TiON0.5. Rutile phase disappears and there are new peaks belong to TiO2 occurred. Compared the peaks of TiON0.7 and TiON0.82 near 25 degree, it supposes to be a little fraction of anatase phase inside TiON0.7. At X=82%, TiON0.82 consists of TiO2. As expected, only TiN is found in the film deposited in 100% N2. XRD results indicate that there is no crystal titanium nitrides found in Ti-O-N films except TiON1 film.

Chemical states of nitrogen in Ti-O-N films were checked by XPS. At the surface N1s spectrum of Ti-O-N films, two peaks at binding energy of 396.6eV and 400.5eV are obtained after resolution by fitting with Gaussian function. The peaks at binding energy of 396.6eV and 400.5eV belong to N3- and molecularly chemisorbed N2 respectively. At the N1s spectrum of Ti-O-N films subsurface, there is only the peak belongs to N3- found. It indicates that molecularly chemisorbed N2 does not exist inside Ti-O-N films and supposes to be no influence to properties of the films. N3- has the influence to properties of the films. The content of nitrogen both on surface and inside of Ti-O-N films increases with X, as shown in Fig.2. The content of N3- inside Ti-O-N films is listed in Table 2.

Optical absorption curves were drawn based on the data obtained by using ultraviolet spectrophotometry. According to Tauc method [4], the band gaps of Ti-O-N films were obtained. With the introduction of nitrogen, both the band gap and the sheet resistance of Ti-O-N films decrease as shown in Fig.3. Compared with 3.18 eV band gap of pure TiO2 film, the band gap and the sheet resistance of Ti-O-N films decrease with X.

Introduction of N3- results in band gap of TiON0.5 narrowing. According to reference [13], the orbit of N2p replaces that of O2p as the top of valence band of TiO2 after N3- doping. Because the orbit of N2p is closer to the
bottom of the conduction band than that of O\textsubscript{2p}, then the band gap of TiO\textsubscript{2} narrowed. For TiON0.7 and TiON0.82 the narrowed band gaps are not only the effect of the introduction of N\textsuperscript{3-} but also an effect of structural changes. The sheet resistance of Ti-O-N films obeyed the same trend. With X increasing, the sheet resistance declined sharply.

Surface energy and water contact angle of Ti-O-N films are shown in Fig.4. The contact angles and the surface energy of Ti-O-N films have no obvious difference and are considered to be independent of X value.

The number of adhesive blood platelets and their morphology as indicator of activation were determined to evaluate the blood compatibility. The degree of deformation of the adhered platelets on the surface of the films can be categorized into four types [3,14,15-17]: I: There are adherent 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 pseudopodia; II*: a portion of platelets exhibit pseudopodium; II**: many platelets showing pseudopodium. III: Adhered platelets are 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 adhere onto the net structure.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Band gap (eV)</th>
<th>Platelet adhesion and activation</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiON0</td>
<td>3.18</td>
<td>II**</td>
</tr>
<tr>
<td>TiON0.5</td>
<td>3.10</td>
<td>III*</td>
</tr>
<tr>
<td>TiON0.7</td>
<td>2.20</td>
<td>III**</td>
</tr>
<tr>
<td>TiON0.82</td>
<td>1.93</td>
<td>IV*</td>
</tr>
<tr>
<td>LTIC</td>
<td></td>
<td>IV*</td>
</tr>
</tbody>
</table>

The results are listed in Table 3. The number of platelets adhered onto TiON0, TiON0.5 and TiON0.7 are much less than TiON0.82 and LTIC. And the degree of deformation (pseudopodium) and aggregation of the adhered platelets on the surface of TiON0, TiON0.5 and TiON0.7 are also less than TiON0.82 and LTIC. The platelet adhesion and activation of TiON0.82 and LTIC are almost at same level. It can be concluded that the platelet adhesion and activation on the surface of Ti-O-N films increase with increasing X value. This result indicates that nitrogen introduction deteriorates the blood compatibility of titanium oxides films.

As for the reactive mechanism between blood and materials, it is still unclear. However, it is widely accepted that the first event of a biomaterial in contact with blood is the adsorption of proteins [1]. Albumin and fibrinogen as proteins with highest plasma concentration also govern the adsorption process [18-20]. If the adsorbed fibrinogen becomes denatured, platelets will be activated and further enhance the cascade reaction of blood coagulation. It has been assumed that a charge transfer to the biomaterial could cause the denaturation of fibrinogen, and this process is related to the electronic structure and properties of the biomaterial [4,21-23]. Fibrinogen has an electronic structure similar to that of a semiconductor, with a band gap of 1.8 eV [4,21-23]. An energy band model can be applied to explain the relationship between fibrinogen denaturation and titanium oxide band structure. Fibrinogen electrons
move from their occupied valence band into the free states of the materials surface and cause the decomposition of fibrinogen to fibrin. According to this hypothesis, a material without holes in the valence band and which has free electrons in the conduction band should exhibit good blood compatibility by prevention of fibrinogen electron transfer to the material and spontaneous fibrin formation.

Nitrogen doping titanium oxides film can be regarded as a semi-conductor whose valence band has an excess of holes and conduction band lacks free electrons. The electrons of the valence band of fibrinogen might transfer more easily into the conduction band of Ti-O-N films. Fibrinogen converts to fibrin after giving off an electron and the platelets are activated. Thus, the blood compatibility of Ti-O-N films are worse than that of titanium dioxide (TiON0).

4. Conclusion

Ti-O-N films with different structures and compositions were synthesized on silicon wafer by reactive unbalanced magnetron sputtering at different X which represents the flux ratio of N2/ (O2+N2). As X increases from 0% to 100%, the structure of the films changes from TiO2 to TiN gradually. Surface energy and water contact angle of Ti-O-N films are not influenced by X. The band gap and the sheet resistance of films decrease with X. The blood compatibility of Ti-O-N films decreases with X. And an energy band model can be applied to explain the relationship between blood compatibility and Ti-O-N films band structure.

Acknowledgements

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Reference