Evaluation of Degradability of CaTiO$_3$ Thin Films in Simulated Body Fluids

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In vitro dissolution behaviors of CaTiO$_3$ thin films deposited with ion beam assisted deposition (IBAD) and sputter-deposition techniques were investigated using Rutherford backscattering spectrometry (RBS) and Auger electron spectroscopy (AES). In vitro test was carried out by immersion in a simulated body fluid at 37°C for 5, 24, and 888 h. The dissolution of titanium ions from CaTiO$_3$ film was almost independent of deposition techniques while that of calcium ions was dependent on those. In the specimens deposited by sputter-deposition, the dissolution rate of the calcium ions increased proportionally with time, and in the case of IBAD, it increased proportionally with the logarithm of time. Furthermore, in IBAD, the dissolution rate of the calcium ions was also intimately related with the total kinetic energy of the titanium ions when implanted. The results reveal that IBAD CaTiO$_3$ coating film makes it possible to control dissolution rate of calcium ions from the film.

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1. Introduction

Titanium alloys are widely used as biomedical and dental materials because of its excellent biocompatibility$^1$ and good mechanical properties.$^2$ Titanium alloys also have good bone conductivity.$^3$ However, improvement of bone conduction of titanium alloys is sometimes demanded from biomedical field such as orthopedics and dentistry. To enhance bone conductivity, titanium alloys are sometimes coated with bioactive ceramics such as hydroxyapatite (HAP).$^5$ Recently, some of the present authors attempted to enhance bone conductivity by depositing of CaTiO$_3$ thin film.$^6$ This method does not form bioactive ceramics directly on titanium but the film promotes the formation of HAP. In this method, calcium dissolution is an important event to promote HAP in hard tissue of human body.$^6$ In order to form HAP rapidly, dissolution rate of calcium must be controlled. There are many reports on bioactive ceramics coating methods, such as sputter-deposition,$^7$ plasma-spraying$^8$ and laser deposition.$^9$ However, the films formed by these methods have a poor bonding between the film and titanium substrate and are dissolved rapidly into body fluids.$^6$ In order to control the dissolution rate of calcium ions, we have coated CaTiO$_3$ thin film by ion beam-assisted deposition (IBAD) and evaluated their properties. It is reported that films deposited by IBAD show high bonding strength$^{10,11}$ and high corrosion resistance.$^{12,13}$ Hence, it is expected that CaTiO$_3$ film deposited by IBAD shows lower dissolution rate of calcium ions than those deposited by other techniques and that the dissolution rate of calcium ions is controlled.

In this paper, CaTiO$_3$ thin films were deposited by IBAD under various conditions such as acceleration voltage of ions and current of ions with simultaneous implantation of titanium ions. The film compositions were quantitatively determined before and after immersion in a simulated body fluid using Rutherford Backscattering spectrometry (RBS) and using Auger electron spectroscopy (AES).

2. Experimental

2.1 CaTiO$_3$ film formation.

CaTiO$_3$ films were prepared on a disk-shape glass-like carbon (GC) substrate by ion beam assisted deposition (IBAD) with titanium ions as assisted ions. For exact evaluation with RBS, GC was employed as substrate. Surface area of the GC substrate was 22 cm$^2$. Details of this IBAD system are described elsewhere.$^6$ The titanium ion implantation voltage was 20 and 30 kV, and the current of implanted titanium ions was 13 and 32 μA. For comparison, the specimen deposited CaTiO$_3$ film without titanium implantation was also prepared. In Table 1, the prepared specimens and their formation conditions were listed. The thickness of deposited films was calculated with sputtering rate of CaTiO$_3$ film as about 100 nm. The range of titanium ion implanted with 30 kV was calculated by TRIM Code as about 17 nm. Therefore, titanium ions hardly reach the substrate when the

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Sputtering rate of CaTiO$_3$</th>
<th>Ti$^+$ implantation</th>
<th>Acceleration voltage of Ti$^+$</th>
<th>Ti$^+$ current at Faraday cup</th>
<th>Total dose of implanted Ti$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPT 1</td>
<td>0.065 A/S</td>
<td>No</td>
<td>—</td>
<td>29 μA</td>
<td>2.7 × 10$^{15}$ atoms/cm$^2$</td>
</tr>
<tr>
<td>SPT 2</td>
<td>0.065 A/S</td>
<td>Up to 30 nm</td>
<td>30 kV</td>
<td>32 μA</td>
<td>9.8 × 10$^{15}$ atoms/cm$^2$</td>
</tr>
<tr>
<td>IBD 1</td>
<td>0.065 A/S</td>
<td>Through the film depth</td>
<td>30 kV</td>
<td>13 μA</td>
<td>4.0 × 10$^{15}$ atoms/cm$^2$</td>
</tr>
<tr>
<td>IBD 2</td>
<td>0.065 A/S</td>
<td>Through the film depth</td>
<td>20 kV</td>
<td>13 μA</td>
<td>4.0 × 10$^{15}$ atoms/cm$^2$</td>
</tr>
</tbody>
</table>
thickness of deposited CaTiO$_3$ film was 17 nm or more. Effects of implanted titanium ions are expected as follows: (1) on the propagation into substrate and formation of ion-mixing layer between CaTiO$_3$ film and substrate and (2) on the propagation into CaTiO$_3$ film and change of the properties of the film. In order to clarify the difference of these two effects, titanium-ion-implanted specimen that only initial 30 nm process was also prepared.

2.2 Conditions of immersion tests.

The specimens were immersed in 44 mL of a simulated body fluids (SBF) at 37°C for 5, 24 and 888 h. The ion concentrations of the SBF used were the same that appeared in a paper by Uchida et al. The SBF was prepared by dissolving reagent-grade CaCl$_2$, KH$_2$PO$_4$, 3H$_2$O, KCl, NaCl, MgCl$_2$, 6H$_2$O, NaHCO$_3$, and Na$_2$SO$_4$ (Nacalai Tesque, Inc) in distilled water. The SBF was buffered at pH = 7.4 with tris(hydroxymethyl)aminomethane ((CH$_2$OH)$_3$CNH$_2$; Nacalai Tesque, Inc) and 1 kmol/m$^3$ HCl. After the allotted immersion period, the specimens were retrieved from fluids, gently rinsed with distilled water, and dried at 40°C.

2.3 Evaluation of the solubility of CaTiO$_3$ film

Since calcium ions were included in the SBF, it was difficult to evaluate the solubility of calcium of CaTiO$_3$ film by analyzing the ion concentration change of SBF. Therefore, the solubility was evaluated by the change of CaTiO$_3$ film itself. Rutherford backscattering spectrometry (RBS) was applied to evaluation. Fig. 1 is a schematic illustration of the measurement by RBS. The 2.5 MeV He$^{++}$ ions were incident perpendicularly to the surface of the specimens and detected at the angle of $\theta = 170^\circ$. In order to clarify the in-depth distribution of elements in CaTiO$_3$ films, Auger electron spectroscopy (AES, JAMP-7100E, JEOL Inc) was also applied.

3. Results and Discussion

3.1 Dissolution of Ti from the CaTiO$_3$ film

Figure 2 shows typical RBS spectrum. All spectrums from CaTiO$_3$ film and substrate are completely separated. Therefore, it is possible to evaluate the area density (number of atoms per square of the unit length) of each constituent element of the CaTiO$_3$ film by integration of each spectral region. In Fig. 3, the qualitative changes of Ti and O in the CaTiO$_3$ film, before and after immersion for 888 h in SBF, are shown, where [Ti] and [O] denoted area density of Ti and O in the CaTiO$_3$ film, respectively. Regardless of Ti-ion implantation conditions, the amounts of dissolved Ti into the SBF are several percent and almost the same as each other before immersion. The amounts of O, [O]$_A$/[O]$_B$, is dependent on Ti-ion implantation conditions. The [O]$_A$/[O]$_B$ values on the SPT 1-3 specimens, where Ti-ions were implanted in the specimens all through the depth are a little increased after immersion.

3.2 Time dependence of the dissolved quantity of Ca

In Figs. 4(a) and (b), the change in the relative quantity of Ca, [Ca]$_A$/[Ca]$_B$, in the CaTiO$_3$ film to immersion time are shown, where [Ca] denotes area density of Ca in the CaTiO$_3$ film. It is apparent that the relative dissolution kinetics of the quantity with immersion time depends on the Ti-ion implantation condition. In IBD 1-3 (implanted all through the film depth), the relative quantity of [Ca]$_A$/[Ca]$_B$ decreased logarithmically with time up to 888 h (Fig. 4a), and about 70% of the Ca before immersion still remained after immersion for 24 h. Furthermore, after immersion for 888 h, it could also be seen that the amounts of the remaining Ca depended on the ion implantation condition, acceleration voltage of ions and current of ions. However, in SPT 1-2, the [Ca]$_A$/[Ca]$_B$ decreased linearly with the immersion time.
respectively. Figure 5 shows relationship between the slope

\[
\frac{[\text{Ca}]_A}{[\text{Ca}]_B} \times 100 \text{ (at%)}
\]

of the relative quantity of Ca for IBD 1-3 in Fig. 4(a) versus log \( t \) and \( E_T \). This relationship is nearly straight and shows that the dissolution rate of the Ca in the CaTiO\(_3\) film is intimately related with the total kinetic energy given by the ion-implantation. These facts suggest that it is possible to control the dissolution rate of the Ca in the CaTiO\(_3\) film by using IBAD technique by changing ion-implantation condition.

### 3.3 In-depth profiles of Ca

Figures 6(a) and (b) show the change in the in-depth profile of SPT 1 and IBD 1 with immersion time, respectively. The intensity of C and O are increased than real intensity by absorption of contaminant. As-prepared SPT 1 and IBD 1 specimens show almost the same in-depth profiles. After immersion for 5 h, in spite of almost the same dissolution quantity (Fig. 4(b)), the in-depth profiles become different in SPT 1 and IBD 1; the Ca in IBD 1 specimen is eluted mainly from the part of specimen surface than that in SPT 1. After immersed for 24 h or 888 h, the Ca concentration in all depth of film decreased uniformly or the Ca is dissolved from the whole region in SPT 1 specimen. On the other hand, in IBD 1 specimen, it occurs mainly near the surface. It is conjectured that this difference is due to the difference in the dissolution rate of the Ca in the CaTiO\(_3\) film which causes the difference in the dissolution behavior. In order to confirm this hypothesis, it is required to investigate further about the change in the CaTiO\(_3\) film caused by ion beam assisting.

### 4. Conclusions

By studying the dissolution mode of the CaTiO\(_3\) film deposited by IBAD technique in a simulated body fluid (SBF), the following conclusions are obtained:

1. The amounts of dissolved Ti from the CaTiO\(_3\) film during soaking in SBF for 888 h is a several percent (at%), and there is no difference between sputter-deposition and IBAD techniques.
2. The dissolution rate of the Ca in the CaTiO\(_3\) film prepared by IBAD technique increases proportionally to logarithm with time, and that prepared by sputter-deposition technique increases proportionally with time.
3. The dominant effect of ion beam assisting in dissolution mode is not formation of ion mixing layer but change in the property of the thin film itself.
4. The dissolution rate of the Ca in the CaTiO\(_3\) film prepared by IBAD technique is related to the total kinetic energy of implanted ions. It is, therefore, possible to control the dissolution rate of the Ca by adjusting the assisting ion beam conditions.
5. The in-depth profile of the CaTiO\(_3\) films after dissolution in SBF for more than 24 h depends on IBAD technique and sputter-deposition technique. In the CaTiO\(_3\) film prepared by simple sputter-deposition technique, the Ca is dissolved generally from all the film thickness, while the Ca in CaTiO\(_3\) film prepared by IBAD technique is dissolved in order from the surface.
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REFERENCES


Fig. 6 In-depth profiles of different immersion time for (a) SPT 1 and (b) IBD 1.