Mechanism of Apatite Formation on Single Crystal Silicon in an Aqueous Solution at Room Temperature

Kotaro HATA, Naoshi OZAWA* and Tadashi KOKUBO**

Maruta Manufacturing Co., Ltd., 4-4-1, Higashikinoso, Yokaichi-shi, Shiga 520-8558
*Department of Fundamental Energy Science, Graduate School of Energy Science, Kyoto University, Yoshida-Honnachi, Sakyou-ku, Kyoto-shi 606-8501
**Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Yoshida-Honnachi, Sakyou-ku, Kyoto-shi 606-8501

Single crystal silicon was soaked in a solution with ion concentrations 1.5 times those of human blood plasma (1.5 SBF) and a bone-like apatite layer formed on it. From analyzing the surface structural change of single crystal silicon and the composition change of solution during soaking, the mechanism of apatite formation was interpreted as follows. The single crystal silicon reacts with 1.5SBF to form a silica gel layer on its surface. The gel layer induces apatite nucleation on its surface and the apatite nuclei grow by consuming calcium and phosphate ions from 1.5SBF. By continuously supplying the ions, a dense and uniform layer of apatite with desired thickness can be formed. This method is promising for developing advanced functional medical devices such as biosensors.

1. Introduction

The present authors showed in earlier work that a dense and uniform bone-like apatite layer with controlled thickness can be formed on many kinds of substrates including ceramics, metals and organic polymers in many shapes including micro spheres, fibers and fabric by the following so-called “biomimetic process” at room temperature and pressure.1)-9) In this process, a substrate is first set in contact with particles of a CaO-SiO2-based glass in a simulated body fluid (SBF) and the composition change of solution during soaking, the mechanism of apatite formation on the single crystal silicon was discussed.

2.1 Preparation of single crystal silicon

A single crystal silicon synthesized by Czochralski (CZ) method and cut into a wafer parallel to the (111) plane, was supplied by Osaka Titanium Co., Ltd. The wafer was cut into a rectangular specimen of 10×15×0.3 mm3 and then a surface of the specimen was abraded with a #400 abrasive plate.

2.2 Imersion into solution

An aqueous solution with ion concentrations of 1.5 times those of SBF (1.5SBF), as shown in Table 1, was prepared by dissolving reagent-grade NaCl, NaHCO3, KCl, K2HPO4·3H2O, MgCl2·6H2O, CaCl2 and Na2SO4 into ion-exchanged distilled water. The surface was examined by thin-film attachment, and for FT-IR measurement, the reflection angle was 75°. These instrument conditions were arranged for characterizing the surface layer approximately 1 µm thick. The cross section near the surface was exa-
mined by energy dispersive X-ray analysis (EDX; Model EMAX-2700, Horiba).

2.4 Ion concentration analysis
After soaking the specimen for various periods of time, concentrations of Ca, P and Si in 1.5SBF were measured using inductively coupled plasma (ICP) emission spectroscopy (Model ICAP-96-953, Nippon Jarrel-Ash). One cm$^3$ of 1 mol·dm$^{-3}$ HCl was added into 30 cm$^3$ of 1.5SBF after specimen soaking and renewal. One cm$^3$ of the solution was drawn out and diluted with 4 cm$^3$ of distilled water for ICP measurement.

3. Results
Figures 1 and 2 show thin film XRD patterns and FT-IR reflection spectra of the surface of the single crystal silicon soaked in 1.5SBF for various periods of time. Assignment of main peaks was made by referring to previously published data.$^{14-16}$ Figures 1 and 2 show that apatite is formed on the single crystal silicon by soaking in 1.5SBF for 2 or more d. During the first day, intensities of the broad peak at 22$^\circ$ in the TF-XRD pattern and the broad reflection peaks at 500, 1100 and 1250 cm$^{-1}$ in the FT-IR spectra increased. They are ascribed to a silica gel. These results indicate that a silica gel layer is initially formed and then an apatite layer is formed on the surface of the single crystal silicon in 1.5SBF.

Figure 3 shows SEM photographs of the surface of single crystal silicon soaked in 1.5SBF for various periods of time. It can be seen from Fig. 3 that apatite starts to form between 1 and 2 d after immersion into 1.5SBF and that a dense apatite layer about 7 µm thick is formed after 7 d.

Figure 4 shows SEM photographs and EDX composition al profiles of the cross sections of the single crystal silicon soaked in 1.5SBF for various periods of time. The presence of the silica gel layer can be detected by the Si profile in Fig. 4. The gel layer is negligible within 1 d after the immersion into 1.5SBF, and appreciably grows between 1 and 2 d. After 7 d, a gel layer 5.7 µm thick is formed between the single crystal silicon and the apatite layer. Figure 5 shows the thickness of the apatite layer formed on the single crystal silicon, which is determined from Figs. 3 and 4, as a function of soaking time in 1.5SBF. This indicates that the thickness of both the apatite and silica gel layers started to increase 1 d after the immersion and saturated after 4 d. This is the case in which 1.5SBF was not renewed. When 1.5SBF

<table>
<thead>
<tr>
<th>Ion Concentration / mmol·dm$^{-3}$</th>
<th>Na$^+$</th>
<th>K$^+$</th>
<th>Ca$^{2+}$</th>
<th>Mg$^{2+}$</th>
<th>Cl$^-$</th>
<th>HCO$^3$</th>
<th>HPO$^4$</th>
<th>SO$^2$</th>
<th>Buffer$^*$</th>
</tr>
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<tbody>
<tr>
<td>SBF</td>
<td>142</td>
<td>5.0</td>
<td>2.5</td>
<td>1.5</td>
<td>148</td>
<td>4.2</td>
<td>1.0</td>
<td>0.50</td>
<td>Buf</td>
</tr>
<tr>
<td>1.5SBF</td>
<td>213</td>
<td>7.5</td>
<td>3.8</td>
<td>2.3</td>
<td>222</td>
<td>6.3</td>
<td>1.5</td>
<td>0.75</td>
<td>1.6Buf</td>
</tr>
<tr>
<td>Blood plasma</td>
<td>142</td>
<td>5.0</td>
<td>2.5</td>
<td>1.5</td>
<td>103</td>
<td>27.0</td>
<td>1.0</td>
<td>0.50</td>
<td></td>
</tr>
</tbody>
</table>

$^*$Buf: (CH$_2$OH)$_3$CNH$_2$ 50 mmol·dm$^{-3}$ and HCl mmol·dm$^{-3}$.
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Fig. 3. SEM photographs of the surfaces of single crystal silicon plates soaked in 1.5SBF for various periods.

Fig. 4. SEM photographs and EDX compositional profiles of the cross-sections of single crystal silicon plates soaked in 1.5SBF for various periods.

was renewed every day, the thickness of the apatite layer and silica gel layers changed with the soaking time, as shown in Fig. 6. The thickness of the apatite layer increased linearly with increasing soaking time from one day after immersion, while that of the silica gel layer was saturated at about 2 mm after 2–3 d. Figure 7 shows an SEM photograph of the surface of the single crystal silicon soaked in 1.5SBF for 8 d with renewing 1.5SBF every day. Figure 8
shows an SEM photograph and compositional profile of a cross section of the single crystal silicon given in Fig. 7. A dense and uniform apatite layer ~17 μm thick is formed on the single crystal silicon through a thin silica gel layer.

Figure 9 shows concentration changes of Ca, P and Si in 1.5SBF during the single crystal silicon soaking time. In this case, 1.5SBF was not renewed. The concentration of Si appreciably increased within one day and then the rate of increase decreased with increasing soaking time. The concentrations of calcium and phosphorus were constant during the first day, and decreased to a plateau after 4 d for P and after 7 d for Ca.

4. Discussion

The decrease of Ca and P concentrations corresponds well to the formation of apatite as detected by TF–XRD, FT–IR and SEM. The Ca/P ratio of the apatite formed on the single crystal silicon is 1.5, which is calculated from the decrease in Ca and P concentrations in 1.5SBF during the soaking. This value means that the apatite formed on single crystal silicon is calcium deficient; since the value is lower than the typical value of 1.67 for stoichiometric hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂).

It is clear from Figs. 1 to 4 that when single crystal silicon...
is soaked in 1.5SBF, a silica gel layer is formed and then a bone-like apatite layer is formed on it. The mechanism of the apatite formation on single crystal silicon is considered as follows. When the single crystal silicon is soaked in 1.5SBF, it reacts with water molecule to form a silica gel layer on its surface and release a part of the hydrated silica (see Fig. 9). This silica gel layer induces the apatite nucleation within one day. It has already been experimentally shown that silica gel rich in Si-OH groups are effective for apatite nucleation. Once the apatite nuclei are formed, they spontaneously grow by consuming calcium and phosphate ions, since 1.5SBF is already supersaturated with respect to apatite. This apatite growth, however, causes a decrease in the ion activity product of apatite in the solution and results in a decrease of growth rate, as shown in Fig. 5, when 1.5SBF is not renewed. However, when 1.5SBF is renewed, the apatite layer continues to grow due to a renewed supply of the calcium and phosphate ions, as shown in Fig. 6. When the apatite layer attains a suitable thickness, the growth of the silica gel layer under the apatite layer is suppressed, since the apatite layer prevents the diffusion of water molecules from the surface to the single crystal silicon. As a result, a dense and uniform apatite layer is formed on the surface of the single crystal silicon as shown in Fig. 7.

5. Conclusions

When single crystal silicon was soaked in a solution with ion concentrations 1.5 times those of human blood plasma (1.5SBF), a bone-like apatite layer formed on it. From analyzing the surface structural change of single crystal silicon and the composition change of solution during soaking, the mechanism of apatite formation was explained as follows. The single crystal silicon reacts with 1.5SBF to form a silica gel layer on its surface. The gel layer induces apatite nucleation on its surface and the apatite nuclei grow by consuming calcium and phosphate ions from 1.5SBF. By continuously supplying the ions, a dense and uniform layer of apatite with desired thickness can be formed. This method is promising for developing advanced functional medical devices such as biosensors.

References