Formation process of apatite layer on titanium-coated silicon wafer surfaces

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Apatite-coated silicon wafers are expected to be utilized for novel biosensors or implants. However, the mechanism and optimum conditions for the formation of an apatite layer on silicon wafer surfaces are unclear. Herein, we examined the effect of pretreating silicon wafers with titanium sputtering and weak alkali aqueous solutions before immersing them in a simulated body fluid (SBF). A week after immersion, silicon wafer surfaces coated with thin titanium layers were covered by hemispherical particles that were produced in a heterogeneous nucleation reaction, whereas untreated silicon wafer surfaces were covered by spherical particles that were produced in a homogeneous reaction. Pretreatment of titanium-coated silicon wafers with 0.1 M NaOH aqueous solution assured heterogeneous apatite formation. Both titanium-coated and untreated silicon wafers were fully covered by the apatite layer after soaking in the SBF for 2–3 weeks. These findings show that pretreatment of silicon wafers with titanium sputtering and weak alkali aqueous solution is effective for obtaining apatite-coated silicon wafers.

Key-words : Apatite, Silicon wafer, Titanium coating, Alkali treatment

1. Introduction

Apatite-coated silicon wafers are expected to be applied in novel biosensors and implants.¹ Some researchers have reported methods for the deposition of apatite crystals on silicon wafer surfaces; for example, Hata et al. showed that apatite particles are formed at ambient temperatures when silicon wafers are soaked in an aqueous solution containing 1.5 times more ions than body fluid after abrading the wafer surface.² Liu et al. reported apatite formation on hydrogen-doped silicon surfaces.³ In this case, negatively charged functional groups such as ≡Si–O¹加快erate apatite formation on the wafer surface.

Titanium metal is also an appropriate substrate for apatite crystal formation because Ti–OH groups combine with Ca²⁺ ions to form amorphous calcium titanate,⁴ which later combines with phosphate ions to form amorphous calcium phosphate. The amorphous calcium phosphate eventually transforms into bone-like apatite. Amin et al. observed apatite formation on TiO₂-coated silicon wafer surfaces from a simulated body fluid (SBF).⁵ Apatite formation was more pronounced on the surfaces of the anastase films compared to those of rutile.

Herein, we observed temporal changes in the apatite-formation process to determine the optimum deposition conditions. First, a titanium-coated silicon wafer and an untreated silicon wafer were immersed in SBF for 3 weeks. Before immersion, the silicon wafers were treated with 0.1, 0.5, or 1.0 M NaOH aqueous solution for 24 h. Then, the morphologies of the silicon wafer surfaces were observed by laser optical microscopy (LOM) and scanning electron microscopy (SEM), and the composition and crystal structure were characterized by energy-dispersive X-ray spectroscopy (EDX) and thin-film X-ray diffraction (XRD).

2. Experimental

2.1 Materials

Sodium chloride, dipotassium hydrogenphosphate, 1 M hydrochloric acid, and tris-(hydroxymethyl)-aminomethane were purchased from Nacalai Tesque, Inc. (Kyoto, Japan). Sodium hydrogen carbonate, potassium chloride, and sodium hydroxide were purchased from Kanto Chemical Co. Inc. (Tokyo, Japan). Magnesium chloride hexahydrate, calcium chloride, and sodium sulfate were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Acetone was purchased from Junsei Chemical Co., Ltd. (Tokyo, Japan). SBF was prepared by dissolving sufficient quantities of reagents to obtain a solution containing Na⁺: 142.0, K⁺: 5.0, Mg²⁺: 1.5, Ca²⁺: 2.5, Cl⁻: 147.8, HCO₃⁻: 4.2, HPO₄²⁻: 1.0, and SO₄²⁻: 0.5 mM before finally adjusting its pH to 7.40.⁶

2.2 Pretreatments and immersion in SBF

Titanium coatings were deposited by sputtering onto silicon wafers (p-type, resistivity: 1–50 Ω cm), on which 750-nm-thick thermally oxidized films were previously formed as a barrier to alloying. A 100-nm-thick titanium film was deposited using a pure titanium target of 50 mm diameter by application of 100-W radio-frequency power under 0.58 Pa pressure of argon gas. The 5 × 5 × 0.6 mm silicon wafers, were ultrasonically washed in acetone and ultrapure water for 5 min each and were dried at 333 K for 3 h. The wafers were then immersed in 0.1, 0.5, or 1.0 M NaOH aqueous solution at 298 K for 24 h. After the samples were taken out of the alkali solutions, they were washed with ultrapure water and immersed in 0.5 mM HCl at 313 K for 24 h. The obtained wafers were dried at 333 K for 24 h. Finally, the silicon wafers were immersed in SBF for 3 weeks at 310 K.
sets of samples were examined to check the repeatability of the apatite formation.

2.3 Characterization of sample surfaces

The surface roughness of the silicon wafers was evaluated by LOM (LEXT OLS4000, Olympus, Tokyo, Japan). The surface morphologies of the silicon wafers before and after treatments were observed by SEM (SU8000, Hitachi High-Technologies, Tokyo, Japan) accompanied by EDX. The observations were achieved under the acceleration voltage of 20 kV. The phase assignment of the outermost surface was performed using thin-film XRD (Smart Lab, Rigaku, Tokyo, Japan) with CuKα radiation (45 kV, 200 mA).

3. Results and discussion

3.1 Effect of alkali treatment

Figure 1 shows SEM images of titanium-coated silicon wafer surfaces, and Table 1 shows the arithmetic average roughness (R_a) and ten-point average roughness (R_10p) obtained by LOM. Significant changes in the morphology on the micron scale were not observed after treatment with 0.1 M NaOH; the surface roughness parameters of the silicon wafer were R_a = 0.04 ± 0.02 μm and R_10p = 0.52 ± 0.12 μm, which are close to those of the pristine silicon wafers. However, we observed fine structures on the scale of several tens of nanometers by SEM [Fig. 1(a)]. For the case of 0.5 M NaOH treatment, pillar-like structures ranging from a scale of several tens to several hundred of nanometers scale were observed on the treated surface with R_a = 0.12 ± 0.01 μm and R_10p = 1.00 ± 0.17 μm. For the case of 1.0 M NaOH treatment, pillar-like structures were also observed on the surface with R_a = 0.24 ± 0.15 μm and R_10p = 2.93 ± 1.31 μm. Figure 2 shows SEM images of the silicon wafer surface. The surface roughness parameters of the silicon wafer treated with 0.1 M NaOH were R_a = 4.68 ± 0.33 μm and R_10p = 39.9 ± 3.87 μm, which are higher than those for native silicon wafer surfaces (R_a = 0.06 ± 0.03 μm and R_10p = 0.74 ± 0.54 μm). Pyramidal structures of 2–5 μm on a side were formed on silicon wafer surfaces when they were treated with 0.5 and 1.0 M NaOH. The surface roughness parameters of silicon wafers treated with 0.5 M NaOH were R_a = 13.3 ± 2.05 μm and R_10p = 154 ± 15.4 μm, and those of wafers treated with 1.0 M NaOH were R_a = 3.11 ± 0.72 μm and R_10p = 40.1 ± 12.1 μm. These results suggest that structures with higher roughness are formed on silicon wafer surfaces as NaOH concentration increases, and that titanium-coating inhibits corrosion of the wafer surface by alkali solution. Silicon substrates are generally corrodible in NaOH aqueous solution by the following reaction:7

\[ \text{Si} + 2\text{NaOH} + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SiO}_3 + 2\text{H}_2 \uparrow \]

While slightly titanium dissolves in NaOH solution, its solubility is much lower than that of silicon. On the other hand, titanium can be oxidized by an alkali to form hydrated titania as follows:8

\[ \text{Ti} + 3\text{OH}^- \rightarrow \text{Ti(OH)_3}^+ + 4e^- \]

\[ \text{Ti(OH)_3}^+ + \text{e}^- \rightarrow \text{TiO}_2 \cdot \text{H}_2\text{O} + 0.5\text{H}_2 \uparrow \]

Simultaneously, the passive TiO_2 layer that exists on the titanium surface reacts with NaOH to form a negatively charged hydrogen titanate anion and/or sodium hydrogen trititanate8,9

\[ \text{TiO}_2 + \text{OH}^- \rightarrow \text{HTiO}_3^- \]

\[ 3\text{TiO}_2 + x\text{NaOH} + (1 - x)\text{H}_2\text{O} \rightarrow \text{Na}_x\text{H}_{2 - x}\text{Ti}_3\text{O}_7 \]

3.2 Formation and identification of apatite layers

Apatite formation was observed after soaking a titanium-coated silicon wafer in SBF for several weeks. Figure 3 shows LOM images of silicon wafer surfaces with and without titanium coating. Highly dispersed hemispherical particles from a few to several tens of micrometers in size were observed for the titanium-coated silicon wafer after soaking in SBF for 1 week [Fig. 3(a)], whereas accumulation of spherical particles was observed for the untreated silicon wafer [Fig. 3(b)]. Characteristic signals of phosphorus and calcium were observed in EDX measurements at 2.01 and 3.69 keV, respectively, as shown in Fig. 4. Figure 5 shows the XRD patterns of (a) an untreated silicon wafer, (b) a titanium-coated silicon wafer, and (c) a titanium-coated silicon wafer after soaking in SBF for 3 weeks. A strong peak attributed to crystalline silicon was observed at 2θ = 70.1° (d = 1.3 Å) in the pattern of the untreated silicon wafer, and some characteristic peaks for titanium were observed at 2θ = 34.9° (d = 2.6 Å) and 38.0° (d = 2.4 Å) in the pattern of the titanium-coated silicon wafer. For the titanium-coated silicon wafer soaked in SBF for 3 weeks without alkali treatment, a characteristic peak for silicon is observed at 2θ = 69.1° (d = 1.4 Å). In a magnified view, some peaks for hydroxyapatite appeared around 2θ = 26°.
and 32°. These patterns suggest that apatite particles formed on the silicon wafer surfaces.

By the way, ion concentrations with respect to apatite in SBF are supersaturated so that homogeneous and/or heterogeneous nucleation of apatite can be induced by losing thermodynamic balance. Homogeneously nucleated apatite in SBF must be spherical and settle out to accumulate on the surface of wafer. On the other hand, the hemispherical particle shape suggests that the apatite is formed by a heterogeneous nucleation mechanism, in which apatite crystallizes preferentially at the interface between the SBF solution and the solid surface. Generally, apatite formed by heterogeneous nucleation is named bone-like apatite. The high adhesion force which adheres the layer strongly to the substrate is caused by the interspaces of the lath-like sodium hydrogen titanate phase, and the layer gradually integrates with the surface to give a dense and uniform composite structure. Although apatite-coated silicon wafers were obtained by soaking untreated silicon wafers in SBF for several weeks, the particle shape of the precipitated apatite was different from that on titanium-coated silicon wafers. Small amorphous particles ranging from a scale of few to several tens of micrometers in size were observed on silicon wafer surfaces that had been soaked in SBF for 1 week [Fig. 3(b)]. These particles may be apatite that was mainly formed by a homogeneous nucleation reaction in SBF because the particle shape was more spherical than that formed by heterogeneous nucleation, and the particles had accumulated before they fully covered the surface. Previous studies have shown that apatite particles obtained by homogeneous nucleation are weakly bonded to titanium surfaces. Therefore, the bonding force of apatite on the silicon wafer is also expected to be weak. Wafer surfaces were completely covered with apatite particles by soaking in SBF for more than 3 weeks under all conditions studied. Characteristic signals of phosphorus and calcium were again observed by EDX.

### 3.3 Effect of titanium coating and alkali treatment on the apatite formation process

Figure 6 shows the effect of alkali concentration and SBF soaking time on apatite formation on wafer surfaces with and without titanium coatings. When three titanium-coated silicon wafers were soaked in SBF after pretreatment with 0.5 or 1.0 M NaOH aqueous solution, the dominant particle shape could not be determined; the first and second wafers were covered by hemispherical and spherical particles, respectively, but apatite particles were not observed on the third wafer. Then, we could not determine the typical condition on the silicon wafer surface. In Fig. 6, we categorized these condition “indeterminable” with question marks. In contrast, when three titanium-coated silicon wafers were soaked in SBF after pretreatment with 0.1 M NaOH aqueous solution, all wafers were covered by hemispherical apatite particles that were formed through a heterogeneous
nucleation mechanism. As shown in Fig. 6(b), apatite particles were also formed on the untreated wafer. However, the particles were all spherical and were generated through a homogeneous nucleation reaction. The difference between titanium-coated silicon wafers and untreated silicon wafers suggests that titanium coating followed by alkali treatment promotes the heterogeneous nucleation of apatite on silicon substrates.

Enhancement of the apatite-forming ability of titanium-coated silicon wafers might be attributable to the microasperity of the coating derived from titanium particle size distribution. Apatite is reported to be formed more easily on surfaces of chemically treated titanium and organic polymers with microasperity due to more favorable surface energy with respect to heterogeneous nucleation. We found that heterogeneous nucleation of apatite on silicon substrates was more favorable surface energy with respect to heterogeneous nucleation.15),16) We found that heterogeneous nucleation of apatite on silicon substrates.