Biomimetic growth of apatite on hydrogen-implanted silicon

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Abstract

Hydrogen in silicon has been widely applied in semiconductor fields. In this paper, the application of hydrogen-implanted silicon wafer in biomedical fields was explored by investigating its bioactivity. Hydrogen implanted silicon wafers were prepared using plasma immersion ion implantation. The surface structures of the $1.4 \times 10^{17}$ cm$^{-2}$ hydrogen-implanted silicon wafers were investigated using atomic force microscopy and transmission electron microscopy (TEM). The hydrogen depth profiles were acquired by SIMS and the crystal quality of the as-implanted silicon was studied by channeling Rutherford backscattering spectrometry (RBS). The bioactivity of the implanted silicon was evaluated using the biomimetic growth of apatite on its surface after it was soaked in simulated body fluid for a period of time. The TEM, SIMS and RBS results indicate the formation of an amorphous hydrogenated silicon ($\text{a-Si:H}_x$) layer has been formed on the surface of the hydrogen-implanted silicon wafer. After immersion in SBF for 14 days, bone-like apatite is observed to nucleate and grow on the surface. With longer soaking time, more apatite appeared on the surface of the hydrogen implanted silicon but our control experiments did not reveal any apatite formation on the surface of the un-implanted silicon wafer, hydrogenated crystalline silicon wafer (with hydrogen, but no amorphous surface), or argon-implanted silicon wafer (amorphous surface but without hydrogen). Our results indicated that the bioactivity of silicon wafer can be improved after hydrogen implantation and the formation of the amorphous hydrogenated silicon ($\text{a-Si:H}_x$) surface also plays a synergistic role to improve the bioactivity.

Keywords: Hydrogen-implanted silicon; Plasma; Bioactivity; Apatite

1. Introduction

Since the discovery of SiO$_2$-based bioglass by Hench et al. in 1969 [1], many attempts have been made to explore the possibility of some silicon-containing materials applied in biological fields, such as wollastonite, silica gel and porous silicon [2–6]. Silicon by itself was generally considered to be nonessential in biochemistry, except in certain primitive organisms like diatoms [7]. However, in the past 30 years, silicon has gradually been recognized as an essential trace element in the normal metabolism of higher animals. Carlisle has shown that silicon is required in bone, cartilage and connective tissue formation as well as several other important metabolic processes [8]. Some researchers have confirmed that silicon is involved in an early stage of bone formation. Hidebrant et al. [9,10] have used modern genetic engineering techniques to demonstrate that certain genes are activated by hydrated silicon. Hydrated soluble silicon will enhance the proliferation of bone cells (osteoblasts) and active cellular production of transforming growth factors [10,11]. Xynos et al. [12,13] have also shown that the critical concentration of ionic products dissolved from the bioactive glass composed of soluble silicon and calcium ions can enhance osteogenesis through direct control over genes that regulate cell cycle induction and progression. Therefore, an increasing number of silicon-containing materials are being studied for applications in biomedical materials and devices.

Hydrogen in silicon has been widely investigated in the semiconductor area. It has been discovered that hydrogen in silicon greatly changes the electrical property of the resultant electronic devices by passivating...
It has been further reported that high dose implantation of hydrogen and subsequent annealing induce splitting of Si, which is utilized in the fabrication of silicon on insulator (SOI) materials [15]. As a result, a large amount of literature reporting the structure and properties of hydrogen in silicon can be found [16–20], but very few research groups have addressed the role of hydrogen in silicon in biological applications. Dahmen and his colleagues [21] have shown that surface functionalization of amorphous hydrogenated silicon (a-Si:H) and amorphous silicon suboxide films (a-SiOₓ:H) by hydrosilylation reaction have been proved to be largely biocompatible. Based on our literature search, the application of hydrogenated silicon to improve the bioactivity or bone conductivity of silicon has pretty much been unexplored, but the materials could have exciting implications in biomedical engineering and biosensor technologies because silicon-based devices often suffer from problems associated with interfacing to the biological environment. The concept of utilizing Si itself as a bioactive miniaturizable packaging material might provide a solution to some of these problems.

In this work, hydrogen was implanted into silicon wafer using plasma immersion ion implantation (PIII). The bioactivity or bone conductivity of hydrogen-implanted silicon was investigated using a simulated body fluid (SBF) soaking test.

2. Experimental methods

Single crystal 〈100〉 silicon wafers measuring 100 mm polished on one side were used in the experiments. The root mean square (RMS) roughness of the polished surface is about 0.215 nm. Hydrogen was implanted into the polished side using PIII in the plasma laboratory of the City University of Hong Kong [22,23]. The background pressure was pumped to 0.6 mTorr and high-purity hydrogen gas was bled into the vacuum chamber to establish a working pressure of 0.5 mTorr. The instrumental parameters are listed in Table 1. Previous results have shown that under these conditions in our instrument, H₃⁺ is the dominated ion species in the plasma [24].

The surface structure and roughness of hydrogen-implanted silicon was investigated using atomic force microscopy (AFM) and cross-sectional transmission electron microscopy (XTEM) was performed to identify the nature of defects produced by ion implantation. The crystalline quality of the as-implanted samples was assessed using channeling Rutherford Backscattering Spectrometry (c-RBS) using an incident beam of 2 MeV H⁺ at a backscattering angle of 170°. Secondary ion mass spectrometry (SIMS) measurements were carried out using a Cameca IMS-4F with a Cs⁺ primary beam and the intensities of ²⁸Si²⁺ and H⁺ ions sputtered from the center of a 150-μm-diameter crater were monitored.

After ultrasonically washed in acetone and rinsed in deionized water, the silicon wafers prior to and after hydrogen-implanted were soaked in a simulated body fluid (SBF) for 14 and 28 days. The SBF solution was not replenished during the soaking procedure. The SBF solution was buffered at pH 7.4 with trimethanol aminomethane-HCl. The ionic concentrations in the solution are nearly equal to those in human body blood plasma, as shown in Table 2 [25].

The surface views of silicon wafers prior to and after soaking in the simulated body fluid were observed using cold field emission scanning electron microscopy (SEM). The structure and phase compositions of the surfaces were analyzed by thin film X-ray diffraction (TF-XRD) at a glancing incident angle of 2°, X-ray fluorescence (XRF) as well as Fourier transform infrared spectroscopy (FTIR).

3. Results

The AFM images of the hydrogen-implanted silicon wafer displayed in Fig. 1 indicate that the surface of the hydrogen-implanted silicon wafer is quite smooth with a

<table>
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<th>Table 1</th>
<th>Implantation parameters</th>
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<tr>
<td>Implantation voltage (kV)</td>
<td>30</td>
</tr>
<tr>
<td>Pulse frequency (Hz)</td>
<td>50</td>
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<tr>
<td>Pulse duration (µs)</td>
<td>500</td>
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<tr>
<th>Table 2</th>
<th>Ion concentration of SBF in comparison with human blood plasma</th>
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<tr>
<td>Na⁺</td>
<td>K⁺</td>
</tr>
<tr>
<td>SBF</td>
<td>142.0</td>
</tr>
<tr>
<td>Blood plasma</td>
<td>142.0</td>
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RMS roughness of about 0.235 nm which is closed to the roughness of the silicon wafer before hydrogen implantation. The cross-section TEM micrograph of the hydrogen-implanted silicon wafer in Fig. 2 reveals the formation of defects. There exists a top amorphous zone (about 60 nm in thickness) and a dense dislocation zone (about 150 nm). The dense dislocation zone is located around the projected range of H$_3^+$. Fig. 3 plots the atomic dislocation density versus depth derived from c-RBS and the hydrogen elemental depth profile acquired by SIMS. Hydrogen is mainly found on the near surface to about 170 nm (~8 at%), which is the projected range of H$_3^+$ obtained from the SRIM code. A total atomic displacement zone (amorphous silicon a-Si) is extended from the top surface to the depth of about 50 nm (slightly different from the TEM results due to calibration and instrumentation issues) followed by a dislocation zone located close to the projected range of H$_3^+$. Hence, the implanted sample consists of a highly hydrogen-doped surface with high crystalline disorder.

Figs. 4 and 5 depict the surface views of the unimplanted and hydrogen-implanted samples after soaking in a simulated body fluid for 14 and 28 days. After 14 days immersion in the simulated body fluid, the surface of un-implanted silicon wafer remains smooth similar to that of a silicon wafer before immersion (Fig. 4a), while some single and clustered ball-like particles are observed on the surface of the hydrogen-implanted silicon surface (Fig. 5a). The surface of silicon wafer is, however, not covered completely. The higher magnification micrograph indicates that they have a coral-like structure composed of many...
sheet-like crystallites (Fig. 5c). After an immersion time of 28 days, the number of these ball-like particles increases, and the surface is totally covered by the newly formed layer (Fig. 5b). In contrast, no new substance can be found on the surface of the un-implanted silicon wafer even after soaking in SBF for 28 days (Fig. 4b).

Fig. 6 shows the XRF spectra of the silicon wafers soaked in simulated body fluid for 14 and 28 days. Calcium and phosphorus cannot be detected on the surface of the un-implanted silicon wafer after soaking for 14 and 28 days (Fig. 6a and b) indicating that no Ca–P layer has formed on the surface. On the other hand, the XRF spectra acquired from the hydrogen-implanted silicon wafer soaked in SBF for 14 days show the existence of calcium and phosphorus on the surface (Fig. 7a). After immersion in SBF for 28 days, more calcium and phosphorus are detected indicating the formation of a denser and thicker Ca–P layer (Fig. 7b). The atomic ratios of Ca to P calculated from the XRF spectra are as follows:

<table>
<thead>
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<th>Element</th>
<th>Wt%</th>
<th>At%</th>
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<tr>
<td>PK</td>
<td>36.72</td>
<td>42.88</td>
</tr>
<tr>
<td>CaK</td>
<td>63.28</td>
<td>57.12</td>
</tr>
<tr>
<td>PK</td>
<td>32.89</td>
<td>38.81</td>
</tr>
<tr>
<td>CaK</td>
<td>67.11</td>
<td>61.19</td>
</tr>
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Fig. 5. Surface views of hydrogen-implanted silicon wafer soaked in SBF for: (a) 14 days, (b) 28 days and (c) the higher magnification of the ball-like particles in (a).

Fig. 6. XRF spectra of silicon wafer soaked in SBF for: (a) 14 days and (b) 28 days.

Fig. 7. XRF spectra of hydrogen-implanted silicon wafer soaked in SBF for: (a) 14 days and (b) 28 days.
spectra of the hydrogen-implanted silicon soaked in SBF for 14 and 28 days are about 1.33 and 1.58, respectively. Our data show that the atomic ratio of Ca to P in the Ca–P layer increases gradually to that of hydroxyapatite (1.67) with longer immersion time in SBF. This indicates that the Ca–P layer formed on the surface of the hydrogen-implanted silicon can crystallize to form hydroxyapatite with increasing immersion time in SBF based on the supporting XRD results that will be discussed as follows.

The XRD patterns obtained from the un-implanted and hydrogen-implanted silicon wafers before and after immersion in SBF for 14 and 28 days are shown in Fig. 8. Only crystalline silicon peaks are observed while no crystalline apatite peaks appear in the XRD patterns of the un-implanted silicon wafer soaked in SBF for 14 days and 28 days (Fig. 8a). Compared with the XRD pattern of the hydrogen-implanted silicon wafer before immersion, the XRD pattern of the hydrogen-implanted silicon wafer soaked in SBF for 14 days reveals obvious changes. One silicon peaks disappears as shown in Fig. 8b, but the newly formed Ca–P layer cannot yet be identified unambiguously. The reason for this is believed to be that the Ca–P layer is not yet crystallized to form apatite and the amorphous structure still exists. After an immersion time of 28 days, the peaks of crystalline apatite can be easily identified in the XRD spectra indicating the formation of a new surface layer composed of crystalline apatite. The broadening of the peaks suggests that the apatite particles formed on the hydrogen implanted silicon wafer are superfine or have low crystallinity.

The FTIR spectra acquired from the hydrogen-implanted silicon wafer before and after immersion in SBF for 14 and 28 days are displayed in Fig. 9. Broad OH\(^{-}\) absorption bands from 3700 to 2500 cm\(^{-1}\) and a weak water absorption band around 1650 cm\(^{-1}\) can be seen in these spectra. Bands between 1400 and 1550 cm\(^{-1}\) are due to the carbonate IR absorption \(v_3\). The peak around 870 cm\(^{-1}\) arises from the both the carbonate and HPO\(_4^{2-}\) ions [26]. The broad bands around 1100 cm\(^{-1}\) is mainly attributed to the phosphate [26]. According to Canham and co-workers [6], a sharp P–O bending mode doublet around 600 cm\(^{-1}\) is indicative of a crystalline phase of hydroxyapatite being present. In Fig. 9, the double peak around 600 cm\(^{-1}\) in the FTIR spectra of the hydrogen-implanted silicon wafer soaked in SBF for 28 days is clearer than that in the hydrogen-implanted silicon wafer soaked in SBF for 14 days.
Our results obtained from the FTIR and TF-XRD showed that carbonate-containing hydroxyapatite (bone-like apatite) forms on the surface of the hydrogen-implanted silicon wafer soaked in SBF, indicating that the hydrogen-implanted silicon wafer has good bioactivity.

4. Discussion

The results obtained from the SBF soaking test confirm that apatite cannot form on the surface of virgin silicon wafers even after soaking in SBF for 28 days, but on the other hand, bone-like apatite can form on the surface of hydrogen-implanted silicon wafer after soaking in SBF for a certain time, indicating the bioactivity of silicon wafer can be improved by implanting hydrogen.

It is well known that the surface plays an important role in the response of the biological environment of the artificial biomedical device. Therefore, it is logical to believe that the improvement of the bioactivity of the implanted silicon wafer results from the modified surface by hydrogen implantation. The results from TEM, RBS and SIMS reveal the presence of an amorphous hydrogenated silicon layer (a-Si:H) after hydrogen PIII.

In order to investigate clearly the formation mechanism of bone-like apatite on the surface of the hydrogen-implanted silicon wafer, two comparative experiments were also conducted. One is to investigate the bioactivity of hydrogenated silicon wafer with no surface damage and the other one is to evaluate the bioactivity of argon-implanted silicon wafer which possesses an amorphous surface but no hydrogen. In our experiments, after the hydrogenated silicon wafer and argon-implanted wafer are soaked in SBF for 28 days, no apatite particles can be found on either surface, indicating poor bioactivity on both samples. Our results suggest that only the formation of an amorphous hydrogenated silicon (a-Si:H) surface can improve the bioactivity of silicon wafer and results in the formation of bone-like apatite on its surface after treatment in SBF. Experimental evidence indicates that the formation of apatite requires that the surface be both amorphous and be hydrogenated. The detailed mechanism as well as further work are being pursued in our laboratory and will be promulgated in due course.

5. Conclusion

Hydrogen-implanted silicon wafers were prepared using plasma immersion ion implantation. The results obtained from TEM, SIMS and RBS indicated that an amorphous silicon with hydrogen (a-Si:H) layer formed on the surface of hydrogen-implanted silicon wafer. After immersion in SBF for 14 days, bone-like apatite was observed to nucleate and grow on the surface. With longer soaking time, more apatite appeared on the surface of the hydrogen-implanted silicon wafer but our control experiments did not reveal any apatite formation on the surface of the un-implanted silicon wafer, hydrogenated crystalline silicon wafer (with hydrogen, but no amorphous surface), or argon-implanted silicon wafer (amorphous surface but without hydrogen). The results obtained from this work indicated that the bioactivity of silicon wafer can be improved after hydrogen implantation. The formation of the amorphous hydrogenated silicon (a-Si:H) surface on the hydrogen-implanted silicon wafer is the key to improves the bioactivity of silicon wafer and results in the formation of bone-like apatite on its surface after it was soaked in SBF for a period.

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References


