Hydrogen plasma surface activation of silicon for biomedical applications

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Abstract

Silicon has gradually been recognized to be an essential trace element in the normal metabolism of higher animals, and the role of silicon in the human body has aroused interests in the biomedical community. In fact, the interactions between silicon-based devices and the human body such as biosensors and microelectromechanical systems (MEMS) often suffer from poor biocompatibility. In this work, hydrogen plasma immersion ion implantation (H-PIII) is conducted to improve the bioactivity or bone conductivity of silicon. In order to investigate the formation mechanism of bone-like apatite on the surface of the hydrogen implanted silicon wafer, two comparative experiments, hydrogenation and argon bombardment, are performed. The H-PIII sample exhibits an amorphous surface consisting of Si–H bonds. After immersion in simulated body fluids, a negatively charged surface containing the functional group (–Si–O2−) is produced and bone-like apatite is observed to nucleate and grow on the surface. The surface of the H-PIII silicon wafer favors the adhesion and growth of osteoblast cells and good cytocompatibility may be inferred.

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1. Introduction

A biosensor is a deliberate and intimate combination of a biomolecule and a man-made transducer. The biomolecule provokes a recognition event, either by binding the analyte or causing the analyte to react, whilst the artificial transducer detects the resulting change in a chemical or physical parameter, causing an electrical signal to be created or modified. The sensing schemes of biosensors can be divided into in vivo, ex vivo and in vitro. In vivo monitoring means that the biosensors are implanted within a tissue (Fraser, 1997a).

Although the design and construction of active implantable medical devices such as biosensors have reached an advanced state of development, in vivo sensing of important clinical parameters is still limited by the host’s reactions against the implant as a foreign body, especially against the outer biomembrane. Consequently, implantation of medical devices or biomaterials may result in injury of tissue and initiation of an inflammatory response. In order to eliminate the inflammation, the commonly-used attempt is to make bioactive and biocompatibility implants (Fraser, 1997b).

The remarkable electronic properties, high mechanical strength and orientation of single-crystal silicon, combined with the ability to grow silicon oxide and nitride films on the surface, have made silicon the ideal choice for microchips including biosensors. In addition, silicon is commonly used as the package materials of biosensors. Silicon-based microelectronics and biosensors have undergone tremendous technical development but the bioactivity and biocompatibility of silicon is relatively not well understood. In fact, the surface biocompatibility of silicon is usually poor and the interaction between silicon-based biosensors and MEMS and the human body may not be desirable (Wise and Najali, 1989; Madou and Tierney, 1993). Long-term issues associated with the packaging and biocompatibility of Si chips have been identified to be the major hurdle (Bowman and Mendl, 1986).

Therefore, it is necessary to improve the bioactivity and biocompatibility of silicon-based microelectronic devices and biosensors to meet clinical needs. Some attempts have been made to improve the bioactivity and biocompatibility of silicon wafers. For instance, Canham reported that apatite could be induced to form on the surface of micro-porous silicon films obtained by wet etching (Canham, 1995). Dahmen et al. have...
shown that surface functionalization of amorphous hydrogenated silicon (a-Si:H) and amorphous silicon suboxide films (a-SiO\text{x}:H) produced by a hydrosilylation reaction are largely biocompatible (Dahmen et al., 2003). The samples of a-Si:H or hydrogenated amorphous silicon suboxides (a-SiO\text{x}:H) were deposited by r.f. PECVD in a capacitively coupled reactor. The ability to form apatite on materials soaked in a simulated body fluid (SBF) is commonly used by biomedical researchers to evaluate its bioactivity. If a positive response can be induced, biocompatible Si biochips can be developed to bond directly with both living tissues and bone.

In this work, single crystal silicon wafers were treated using hydrogen plasma immersion ion implantation (PIII) to improve the bioactivity and biocompatibility. In order to fathom the formation mechanism of bone-like apatite on the surface of the hydrogen implanted silicon wafer, two comparative experiments, hydrogenation and argon bombardment, were also conducted.

2. Materials and methods

Hundred millimetres diameter single crystal (1 0 0) silicon wafers polished on one side were used in the experiments. Hydrogen was implanted into the polished side using plasma immersion ion implantation (PIII) in the Plasma Laboratory of the City University of Hong. The details of the hardware and experimental parameter can be found elsewhere (Chu et al., 1996, 1997; Liu et al., 2004). In order to investigate clearly the formation mechanism of bone-like apatite on the surface of the hydrogen implanted silicon wafer, hydrogenation and argon PIII were conducted. The sample holder was subjected to a negative bias of −300 eV and heated to 320–380 °C during hydrogenation for 1.5 h. Argon bombardment was conducted under a negative bias of −10 kV and argon was ionized using radio-frequency of 1000 W for 30 min.

The micro-Raman spectra of the H-PIII, argon bombarded and hydrogenated silicon wafers was acquired in the back-scattering mode using a DILOR-yLSA LabRAM 010 system equipped with an unpolared HeNe laser. The excitation line wavelength was the 632.8 nm and the laser power was 6.4 mW. The crystalline quality of the samples were assessed using channeling Rutherford backscattering spectrometry (c-RBS) using 2 MeV He\textsuperscript{+} and a backscattering angle of 170°.

Contact angle measurements were performed on the solid surface using distilled water. The contact angles of the test liquids on the sample surface were measured by the sessile drop technique using a contact angle goniometer (JY-82, China). The accuracy of this technique is typically ±2°. Results are the means of five measurements taken on different regions of the sample surface. To avoid cross contamination of liquids, a dedicated microsyringe was used for each liquid.

After ultrasonically washed in acetone and rinsed in deionized water, the silicon wafers prior to and after H-PIII, hydrogenation and argon bombardment were soaked in a simulated body fluid (SBF) for 28 days to investigate their bioactivity. The SBF solution was buffered at pH 7.4 with trimethanol amino-methane–HCl. The ionic concentrations in the solution are nearly equal to those in human body blood plasma (Kokubo et al., 1990). The surface view of the H-PIII silicon wafer after soaking in the simulated body fluid was 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° and Fourier transform infrared spectroscopy (FT-IR).

A modified human osteoblast (HOB) cell line (OPC-1) was used to evaluate the cytocompatibility of the H-PIII samples. Approximately 10\textsuperscript{5} cells/cm\textsuperscript{2} OPC-1 were cultured on each 10 mm × 10 mm silicon sample. The cells were maintained at 37 °C under an atmosphere of 5% CO\textsubscript{2} and 95% air. The culture medium was changed every other day. After culturing for 7 days, the samples were fixed in 2.5% glutardehyde in a 0.1 M sodium cacodylate buffer (pH 7.4) for 1 h. After rinsing with phosphate-buffered saline (PBS) (3 × 10 min) and dehydrating in a grade ethanol series, the degree of cell spreading and propagation was determined employing SEM.

3. Results

Fig. 1 plots the atomic dislocation density versus depth derived by channeling-RBS from the H-PIII and argon...
bombarded silicon samples. A total atomic displacement zone (amorphous silicon a-Si, atomic dislocation density is about $5 \times 10^{22}$/cm$^2$) is extended from the top surface to a depth of about 50 nm. Hence, the H-PIII and argon silicon wafer consists of a highly hydrogen-doped surface with high crystalline disorder.

The Raman spectra (400–4000 cm$^{-1}$) obtained from the H-PIII, hydrogenated and argon bombarded silicon wafers shown in Fig. 2a reveal that the vibrational peaks around 520 cm$^{-1}$ corresponding to the Si–Si bond is symmetrical in the hydrogenated sample, whereas it is asymmetrical in the H-PIII and argon bombarded samples. It is also evident that the silicon has been partially disordered by hydrogen implantation and argon bombardment. The Si–H peak around 2000 cm$^{-1}$ can be discerned in the higher resolution Raman spectrum (400–1500 cm$^{-1}$) acquired from the H-PIII silicon wafer (Fig. 2b). The Si–H peak cannot be found in the Raman spectrum of hydrogenated silicon wafer.

![Fig. 3. Contact angle of the untreated, H-PIII, hydrogenated and argon bombarded silicon wafers with water as the test liquid.](image)

**Fig. 3.** Contact angle of the untreated, H-PIII, hydrogenated and argon bombarded silicon wafers with water as the test liquid.

**Fig. 4.** Surface view of the H-PIII silicon wafer after soaking in SBF for 28 days.

**Fig. 5.** TF-XRD patterns of the H-PIII silicon wafer after soaking in SBF for 28 days.

**Fig. 6.** FT-IR spectrum of the H-PIII silicon wafer after soaking in SBF for 28 days.

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Fig. 3 shows the contact angle of the untreated, H-PIII, hydrogenated and argon bombarded silicon wafers using water as the test liquid. All of these samples are hydrophilic. Compared with the untreated silicon wafer, the decrease in the contact angle observed on the hydrogenated sample may result from the formation of Si–OH on its surface, since Si–OH is more hydrophilic than Si–O–Si which is generally formed on the untreated silicon wafer in air (Fan et al., 2000). The increase in the contact angle of the H-PIII and argon bombarded silicon wafers is believed to be due to the formation of disordered surface structure, which will result in higher surface energy.

Fig. 4 depicts the surface view of the H-PIII silicon wafer after soaking in SBF for 28 days. After 28 days of immersion in SBF, the surface is totally covered by the newly formed layer. Results obtained by TF-XRD (Fig. 5) and FT-IR (Fig. 6) show that the newly formed layer is composed of carbonate-
containing hydroxyapatite, indicating that the H-PIII silicon wafer has bioactivity. In contrast, no new substance can be found on the surface of the untreated, hydrogenated, and argon bombarded silicon wafers. Our results show that the bioactivity of these samples is independent on their hydrophilicity.

Fig. 7 shows the surface view of the H-PIII silicon wafer on which OCP-1 cells have been seeded for 7 days. The cells exhibit good adhesion and spreading on the H-PIII silicon wafer surface. The surface is almost covered by human osteoblast cells. This suggests that the surface of the H-PIII silicon wafer is favorable to the adhesion and growth of osteoblast cells and good cytocompatibility may be inferred.

4. Discussion

It is well known that the surface plays an important role in the response of the biological environment of the artificial biomedical device. 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.

Hydrogen is known to interact with silicon in a wide variety of ways, including passivating the surface, deactivating dopants, and passivating shallow as well as deep levels. In our H-PIII silicon wafer, many dangling bonds are produced (Wang et al., 2001), and the surface of the silicon wafer exhibits an amorphous network with disorders and defects. In the H-PIII silicon wafer, hydrogen passivates dangling bonds by forming Si–H bonds. When the H-PIII silicon wafer is soaked in the SBF solution, the following reactions are believed to occur. The amorphous hydrogenated silicon (a-Si:H) surface can improve the bioactivity and biocompatibility of silicon wafer. Afterwards, the silanol (≡Si–OH) reacts with the hydroxyl ion to produce a negatively charged surface with the functional group (≡Si–O−) as follows:

\[ \equiv\text{Si} – \text{OH} + \text{OH}^- \rightarrow \equiv\text{Si} – \text{O}^- + \text{H}_2 \text{O} \]

The formation of negatively-charged surface on bioceramics and bioglasses is generally regarded to be important to the precipitation of apatite (Li and Zhang, 1990; Li et al., 1994; Takadama et al., 2001). Due to the formation of the negatively-charged surface, the calcium ions in the SBF solution are attracted to the negative charged surface site of the silicon wafer. This is followed by the arrival of HPO\(_4^{2-}\) resulting in a hydrated precursor cluster consisting of calcium hydrogen phosphate. After the precursor clusters are formed, they spontaneously grow by consuming calcium and phosphate ions from the surrounding body fluid. The calcium phosphate phase that accumulates on the surface of the silicon wafer is initially amorphous. It later crystallizes to a carbonate-containing hydroxyapatite (CHA) structure by incorporating carbonate anions from the solution within the amorphous calcium phosphate phase.

Generally, all cells are enclosed by a layer of hydrated biopolymer. Thus, the adherent properties of cells to an ideal solid planar substrate can be deduced partly from the water contact angle (Neumann et al., 1983). A hydrophilic surface is suitable for the adhesion and spreading of cells. Therefore, in this work, the surface of the H-PIII silicon wafer is favorable to the adhesion and growth of osteoblast cells. However, it should be noted that cell adherence is also affected by many other biological interactions, and some of them may overwhelm the effects of hydrophilicity.

5. Conclusion

Hydrogen plasma immersion ion implantation is used to improve the bioactivity and biocompatibility of silicon wafer. An amorphous silicon with hydrogen (a-Si:H) layer forms on the surface of H-PIII silicon wafer. After 28 days of immersion in SBF, carbonate-containing hydroxyapatite (bone-like apatite) forms on the surface of the H-PIII silicon wafer, indicating that the H-PIII silicon wafer has bioactivity. In contrast, no new substance can be found on the surface of untreated, hydrogenated, or argon bombarded silicon wafers. The bioactivity of these samples is independent on their hydrophilicity. In addition, the surface of the H-PIII silicon wafer is favorable to the adhesion and growth of osteoblast.

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References


