Recent Developments of Plasma Immersion Ion Implantation (PIII) in Surface Modification and Engineering

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Abstract
Plasma immersion ion implantation (PIII) has been shown to be an effective technique for surface modification due to its high efficiency and large-area processing capability. In this work, the recent breakthroughs, developments and applications of PIII are presented. Works on Si-based and polymeric materials show excel surface characteristics in terms of biocompatibility, bioactivity, and wettability. For example, hydrogen plasma implantation into single-crystal silicon gives rise to high bioactivity and growth ofapatite when immersed in SBF solutions. Amido-materials of Nylon-6 plasma implanted with a gas mixture of oxygen and nitrogen also demonstrate great improvement in the surface wetting properties due to the formation of polar functional groups of amine, alcohol and carbonyl groups. In addition, the formation of metal carbides and fluorides in fluorine-based Teflon materials by metal implantation enhances the surface energy.

1. Introduction
Plasma immersion ion implantation (PIII) was first introduced in the 1980’s to circumvent the line-of-sight restriction of conventional beam-line ion implantation (BLII). PIII offers a number of advantages, such as high efficiency, large area processing, treatment of irregular-shaped targets, as well as small instrument footprint. Recent research focuses of PIII are biomaterials and polymeric materials. In this article, hydrogen implantation of silicon-based materials to enhance surface biological properties, gas and metal implantation of Nylon and Teflon to improve surface wetting properties are presented.

2. Surface bioactivity of hydrogen implanted silicon and its mechanism
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 interest in the biomedical community. In fact, the interaction between silicon-based devices and the human body, such as biosensors and MEMS, often suffer from poor biocompatibility. Hydrogen plasma immersion ion implantation (H-PIII) has been conducted to improve the bioactivity of silicon and the mechanism is also proposed. The instrumental parameters for implantation are listed in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Implantation voltage (kV)</td>
<td>30</td>
</tr>
<tr>
<td>RF Discharge power (W)</td>
<td>1400</td>
</tr>
<tr>
<td>Pulse frequency (Hz)</td>
<td>50</td>
</tr>
<tr>
<td>Implantation time (mins)</td>
<td>20</td>
</tr>
<tr>
<td>Pulse duration (µs)</td>
<td>500</td>
</tr>
<tr>
<td>Implantation dose (cm⁻²)</td>
<td>~ 1.4 x 10¹⁷</td>
</tr>
</tbody>
</table>

After ultrasonically cleaned in acetone and rinsed in deionized water, the samples were soaked in a simulated body fluid (SBF), which was buffered at pH 7.4 with trimethanol aminomethane-HCl and the ionic concentrations in the solution are nearly equal to those in human blood plasma. The cross-sectional TEM micrograph of the hydrogen-implanted silicon in Fig. 1 discloses the formation of defects with a top amorphous zone and a dense dislocation zone. After 14 days and 28 days immersion in SBF, the surface of un-implanted silicon remains smooth similar to that of a silicon before immersion (Fig. 2). On the other hand, the increase amount of the crystalline hydroxyapatite is found on the hydrogen-implanted silicon with increasing the immersion time in SBF (Fig. 3). The structure of hydroxyapatite is in the form of coral-like composed of many sheet-like crystallites. It is well know that the surface plays an important role in the response of the biological environment and it is believed that the enhancement of bioactivity of silicon results from...
the hydrogen induced surface modification. Our TEM result reveals the presence of an amorphous hydrogenated silicon layer (a-Si:H) after hydrogen implantation. In order to have a better understanding of the formation mechanism of apatite on the hydrogen modified surface of silicon, two comparative experiments have also been conducted. One is to hydrogenate silicon with no surface damage and the other is to bombard silicon for amorphous with argon but no hydrogen. There is no apatite particles found on those sample surface after soaked in SBF for 28 days. Experimental evidence has so far suggested that the formation of apatite requires that the surface be both amorphous and be hydrogenated.

The XTEM micrograph in Fig. 4 discloses that the surface apatite layer on hydrogen-implanted silicon is composed of polycrystalline and amorphous apatite. The atomic ratios (Ca/P) obtained by EDS in area A, B and C are 2.69, 1.83 and 1.42, respectively, indicating that calcium accumulation on the silicon wafer takes place prior to that of phosphorus. The HRTEM micrograph in Fig. 5 shows that the (100) plane of the apatite has a spacing of about 0.82 nm. After hydrogen PIII treatment, a disordered silicon surface containing Si-H bonds is produced. During immersion in SBF, the Si-H bonds on silicon react with water to produce a negative charged surface containing the functional group (≡Si-O) by the following reactions:

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

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

The calcium ions in the SBF solution are attracted to the negatively charged surface site of the silicon 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.
3. Wetting properties of gas and metal implanted polymers

Polymeric materials have unique properties such as low density, light weight, and high flexibility and are widely used in various industrial sectors. However, the inert nature of most polymeric materials creates challenges in many applications that demand specific surface characteristics such as those required by inking and printing processes, wetting and adhesion for coatings, biomaterials, and certain types of composite materials. Hence, surface modification of polymeric materials plays an important role in that selected surface properties can be optimized while the favorable bulk attributes of the materials can be retained. In this study, we investigate the effects of nitrogen and oxygen plasma immersion ion implantation on the chemical and physical changes on the surface of Nylon-6 and metal implantation on the change of surface composition and surface energy of Teflon.

3.1 Nitrogen- and oxygen-implanted Nylon-6

The treatment conditions of Nylon-6 are listed in Table 2. The surface chemical states and wetting properties of control and implanted samples are examined by XPS and sessile drop method, respectively. After PIII, it can be observed that the asymmetric C 1s peak (Fig. 6) shifts toward a high binding energy in all the treated samples. It implies that the polymer chains have been broken and the functional groups on the surface have been rearranged and re-established. When Nylon-6 is subjected to high-energy ion bombardment, reactive defects are created on the surface resulting in hydrogen abstraction, C-C bond breaking, and incorporation of reactive nitrogen and oxygen species to form amine [>C-NH₂], alcohol [R-CH₂-OH], and/or carbonyl [C=O] groups. Bond breaking in the chain leads to two fragments that can form various functional groups on the surface according to the following sequences:

\[
\begin{align*}
\text{R-CH}_2\text{-CO-NH-CH}_2\text{R'} & \rightarrow \text{R-CH}_2^* + \text{R'}\text{-CH}_2\text{-NH-CO}^*, \\
\text{R-CH}_2^* & \rightarrow \text{N} \rightarrow \text{R-CH=N-H or R=CH-NH}_2, \\
\text{R-CH}_2^* & \rightarrow \text{O} \rightarrow \text{R-CH}_2\text{-OH}, \\
\text{R-CH}_2^* & \rightarrow \text{O} \rightarrow \text{R-CH=O}.
\end{align*}
\]

![Figure 6. XPS C 1s core level spectra acquired from the control and plasma-implanted samples: (a) control; (b) sample # 2; (c) sample # 3; (d) sample # 4.](image-url)
Table 3. Water contact angles measured from the control and plasma-implanted samples.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Water contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td># 1</td>
<td>66.1</td>
</tr>
<tr>
<td># 2</td>
<td>58.9</td>
</tr>
<tr>
<td># 3</td>
<td>52.6</td>
</tr>
<tr>
<td># 4</td>
<td>26.1</td>
</tr>
</tbody>
</table>

The wetting properties of control and plasma-implanted samples are determined using the sessile water drop method by measuring the contact angle between the sample surface and water surface and the results are listed in Table 3. In contrast to the contact angle of 66.08° observed on the control sample, the contact angles markedly diminish after plasma implantation. Sample # 4 implanted using a high ratio of oxygen mixture exhibits the greatest improvement in the hydrophilicity as illustrated in Fig. 7. The enhancement of the wetting properties can be explained by the formation of polar functional groups thereby increasing the surface free energy of the polymer surface and leading to enhanced adhesion and wetting due to better interaction with water molecules. Comparing the roles of the various newly-formed surface functional groups, the amide group is relatively not reactive and therefore may not contribute much to the adhesion and wetting improvement. The increase of the imine, amine, alcohol, and carbonyl groups on the plasma-implanted surface appears to be the main reason for the wetting enhancement. Our results also indicate that nitrogen implantation produces mainly imine and amine groups on the Nylon surface while a gas mixture of nitrogen and oxygen in the plasma creates preferentially more alcohol and/or carbonyl groups. Since alcohol and carbonyl groups are more polar than that of the imine and amine groups, better wetting properties can be achieved in the mixed-gas plasma treatment. Overall, it is clear that plasma immersion ion implantation can result in dramatic change in the surface chemistry of polymers by introducing favorable functional groups. Coupled with high-energy ion bombardment, sufficient bond breaking and desorption of low molecular weight species occur thereby producing a different chemical structure that gives rise to the enhanced surface properties.

3.2 Cu-, Ni- and Co-implanted Teflon

![Figure 7](image1.png)

Figure 7. Photograph of the water drop on the control and ion-implanted sample: (a) control; (b) sample # 4.

![Figure 8](image2.png)

Fig. 8. C 1s core level spectra acquired from the untreated Teflon and metal implanted Teflon.

![Figure 9](image3.png)

Fig. 9. F 1s core level spectra measured from the untreated Teflon and metal implanted Teflon.
Metal implantation is conducted using cathodic arc plasma source with ~20 kV implantation voltage, 250µs arc pulse duration and 30 Hz repetition frequency. The implantation dose determined by RBS is about $7.5 \times 10^{15}$ cm$^{-2}$. The chemical states obtained by XPS (Fig. 8) reveal that the principal peak (C-F bond at BE = 292.4 eV) and secondary peak (C-C bond at BE = 285.02 eV) are not detected after metal PIII. In all the implanted specimens, the C 1s peak shifts to a low binding energy and signifies the formation of metal carbides. Besides, the F 1s (Fig. 9) peak shift to a low binding energy after metal implantation is due to the formation of fluorine anion species. The deconvoluted components of F 1s peak are corresponded to different metal fluoride states.

The wetting properties of the specimens were investigated using contact angle measurements. Six test liquids with known surface tension components were applied. In general, wettability is the ability of a liquid to adhere to a solid and spread over its surface to varying degrees. Normally, the classical model provided by Thomas Young suggests that

$$\gamma_{SV} = \gamma_{LV} \cos \theta + \gamma_{SL}$$

where $\theta$ is the contact angle, $\gamma_{SV}$ is the surface tension of the solid in contact with air, $\gamma_{LV}$ is the surface tension of the liquid in contact with air, and $\gamma_{SL}$ is the surface tension between the solid and the liquid. The solid surface tension can be compiled into intermolecular attraction of polar interaction $\gamma^p_s$ and dispersion interaction $\gamma^d_s$ as

$$\gamma_s = \gamma_s^d + \gamma_s^p$$

Figure 10 shows an obvious decrease in the contact angle measured on all the treated specimens. The Co-implanted specimen exhibits the lowest contact angle. The decrease of the contact angle and improvement of wetting property can be attributed to the change of physical and chemical properties of the surface after ion bombardment. The surface energy of a solid is determined by the intermolecular attraction of polar interaction and dispersion interaction as described in the equation. Any changes in these two interaction components can result in alteration of the surface energy. Fig. 11 shows the increase of both the polar and dispersion interactions after metal ion implantation. The XPS chemical states shifts shown in the C 1s and F 1s core level spectra reveal the formation of metal carbides and metal fluorides on

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Surface energy (nJ/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>22.33</td>
</tr>
<tr>
<td>Co-implanted</td>
<td>38.22</td>
</tr>
<tr>
<td>Ni-implanted</td>
<td>36.15</td>
</tr>
<tr>
<td>Cu-implanted</td>
<td>36.29</td>
</tr>
</tbody>
</table>
the surface. The structure of these metal carbides and fluorides are totally different from that of high molecular weight polymer chains thereby changing the dispersion component. Moreover, the electron cloud distribution of the ionic bonds of the carbides and fluorides results in a higher polar effect than that of covalent bonds in C-C and C-F. Combining these two effects as shown in Fig. 11 and based on the equation of solid surface tension, it is not difficult to understand the enhancement of the surface energy of the implanted specimens as shown in Table 4.

4. Conclusion

Hydrogen plasma-implanted silicon and gas and metal plasma-implanted polymeric materials lead to more superior surface bioactivity and wetting properties. In our silicon experiments, the formation of an amorphous hydrogenated silicon (a-Si:H) surface on the hydrogen implanted silicon appears to be key to the improvement of the bioactivity of silicon and the formation mechanism of apatite on silicon has been studied. In our polymer work, the formation of the proper functional groups on Nylon-6 and metal carbides and fluorides on Teflon is the main reason for the enhancement of surface wetting properties.

Acknowledgments

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References