Influence of silicon concentration on the haemocompatibility of amorphous carbon

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Abstract

Amorphous carbon (a-C) has good blood compatibility and has been proposed as a coating material for blood contacting devices such as heart pumps and stents. In this study, unhydrogenated a-C films with different silicon concentrations were synthesized by magnetron sputtering, and the corresponding evolution of the surface energy and compatibility with blood were analysed. The incorporation of silicon not only decreased the sp²-hybridized carbon bonding configurations, but the static evaluation of the films incubated in human platelet-rich plasma also showed a decrease in platelet adhesion. Bonding structure and surface energy were determined to be factors contributing to the improved haemocompatibility.

Keywords: Silicon-incorporation; Amorphous carbon; Bonding structure; Surface energy; Human platelet adhesion; Haemocompatibility

1. Introduction

Amorphous carbon (a-C) has good blood compatibility [1–6] and may be used to coat poorly haemocompatible materials for devices in contact with blood. It also offers good mechanical properties such as high hardness and elastic modulus and low coefficient of friction [7]. However, high intrinsic stress inherited during the synthesis cannot be avoided, as it is the by-product of the formation of the diamond-like phase in the a-C [8]. This stress poses a major challenge for the intended usage, as film delamination can occur. The intrinsic stress of a-C films can be reduced by incorporating a small amount of silicon [9,10]. Okpalugo et al. [11] have studied hydrogenated a-C films with silicon-doping levels of less than 10 at%, and showed improved haemocompatibility with decreased platelet count for the doped films. Study on unhydrogenated a-C containing silicon showed that the quantity of adhering platelets was largely influenced by the surface energy of the film [12]. Besides changing deposition parameters or post-deposition treatment, the surface energy can be tuned by altering the concentration of the dopant. In this study, we investigate the influence of silicon concentration on the surface energy of the coatings, and the resulting blood compatibility.

2. Methodology

2.1. Film deposition and surface roughness

Silicon-incorporated unhydrogenated a-C films were sputtered from graphite (99.995% purity) and silicon (99.999% purity) targets on (1 0 0) monocrystalline silicon wafers using E303A Magnetron Sputtering System. Prior to deposition, the wafers were chemically cleaned in a piranha bath (a 3:1 mixture of concentrated sulphuric acid with hydrogen peroxide for removing organic residues) and treated with Ar plasma for 20 min at a radio frequency (RF)-induced substrate bias of −300 V to remove the surface oxides. The graphite target power density was 7.4 W/cm², and the silicon target power density was 2.5 W/cm². The base pressure (4.5 × 10⁻¹ Pa), process pressure (800 × 10⁻³ Pa), Ar flow rate (50 sccm) and substrate bias voltage (−10 V) all remained constant. The surface morphology was characterized by a Shimadzu 9500J2 atomic force microscope under constant force in contact mode.

2.2. X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy

The atomic concentration of Si and C were determined by XPS using the Kratos AXIS X-ray photoelectron spectrometer equipped with a monochromatic Al-Kα (1486.71 eV) X-ray radiation operating at 15 kV
and with a vacuum of $10^{-8}$ Pa. The bonding of a-C(Si) was characterized by Raman spectroscopy using Renishaw Raman Spectroscope RM1000 excited with a HeNe laser at a wavelength of 633 nm and laser power of 1 mW. The peak deconvolution was performed using Gauss–Lorentz distribution function, and the fitted curves have a reduced $\chi^2$ of 1.2 or less to ensure convergence.  

2.3. Surface energy determination

The surface free energy of the films was determined by contact angle measurements. The Lifshitz–van der Waals (LW)/acid–base (van Oss) approach [13] was employed to interpret the contact angle measurements. In this method, the surface tension is differentiated into three components: the apolar LW component, the polar acid (+) and the base (−) components. The “acid” component is also called the acceptor because it is positively charged, thus is ready to accept electrons; the “base” component is also called donor because it is negatively charged, thus has extra electrons to give away. The total surface tension is given by

$$\gamma_{\text{tot}} = \gamma_{\text{LW}} + 2\sqrt{\gamma_{\text{LW}}^2 + \gamma_{\text{sv}}^2 + \gamma_{\text{lv}}^2}.$$  

where $\gamma_+$ is the donor and $\gamma_-$ is the acceptor part of the surface energy. Taking Young’s equation: $\gamma_\text{lv} \cos \theta = \gamma_\text{lv} + \gamma_\text{sf}$ [14] into consideration (where $\theta$ is the measured contact angle, $\gamma_\text{lv}$, $\gamma_\text{sf}$ and $\gamma_\text{sp}$ are the liquid–vapor, solid–vapor and solid–liquid interfacial tension, respectively), the LW/acid–base equation can be written as follows:

$$\gamma(1 + \cos \theta) = 2\sqrt{\gamma_{\text{LW}}^2 + \gamma_{\text{sv}}^2 + \gamma_{\text{lv}}^2}.$$  

Eq. (2) can be used to determine the three surface tension components ($\gamma_{\text{LW}}, \gamma_{\text{sv}}$ and $\gamma_{\text{lv}}$) by measuring contact angles and solving three simultaneous equations. To do this, three liquids of known surface tension are required. We used deionized water, formamide and diiodomethane. The surface tension values of these liquids can be found in Table 2 of [12]. The bonding of a-C(Si) was characterized shows the decrease in the relative intensity of the D-peak. The breaking of the sp² sixfold aromatic rings bonding structure will cause a decrease in the intensity of the D-peak, since the present of the D-peak is due to the present of the sp² aromatic rings [17]. This increases the overall disordering of the C-network, and enhances the chance of sp³ formation. The decrease in $I_D/I_G$ intensity ratio with increasing Si corresponds to the decrease in the average crystallite size of sp³-bonded clusters [17], as well as the increase in sp³ fraction [18]. The disordering and loss of aromatic bonding cause the amorphous-carbon signature peak to downshift [17,19], and this phenomenon is

3. Results and analysis

3.1. Bonding and surface roughness

Fig. 1 shows the Raman spectra of the a-C(Si) films. The Raman spectra were deconvoluted into G (graphitic) and D (disorder) peaks, where the D-peak is the shoulder of the G-peak at lower wavenumbers. Fig. 2 clearly shows the decrease in the relative intensity of the D-peak. The breaking of the sp² sixfold aromatic rings bonding structure will cause a decrease in the intensity of the D-peak, since the present of the D-peak is due to the present of the sp² aromatic rings [17]. This increases the overall disordering of the C-network, and enhances the chance of sp³ formation. The decrease in $I_D/I_G$ intensity ratio with increasing Si corresponds to the decrease in the average crystallite size of sp³-bonded clusters [17], as well as the increase in sp³ fraction [18]. The disordering and loss of aromatic bonding cause the amorphous-carbon signature peak to downshift [17,19], and this phenomenon is
evidential in Fig. 1, which show the downshifting of the asymmetrical peak to lower wavenumbers with increasing Si concentration. The width of G peak scales with disorder, and corresponds to the crystallite size of the sp²-bonded clusters. As shown in Fig. 2, the FWHM of G peak increases; therefore, it further substantiates the results on the increase network disordering and decrease sp² crystallites. Si atoms preferentially substitute the sp²-hybridized C atoms during sputter implantation; the incorporation of Si will break the sp²-hybridized aromatic ring bonding structures. This removes two \( \pi \) bonds per substituted C atom and thus promotes the formation of sp³-hybridized C–C bonding configuration. XPS also shows a decrease in the sp²-hybridized C bondings [20].

### 3.2. Surface energy and haemocompatibility

The corresponding surface energies are presented in Fig. 4. The dispersive component of surface energy initially decreases at low Si concentration and reached a minimum at Si concentration of \( \sim 16.6 \text{ at} \% \), and then follows by a rise as the Si concentration increases further. The polar component, on the other hand, increases with Si concentration.

For hydrogenated a-C, there are relatively fewer unfused bonds at the surface when most are terminated by H, which has only one electron available for bonding. This reduces the tendency for the surface atoms to bond with other atoms in the atmosphere. Unlike hydrogenated a-C, the surface atoms of hydrogen-free a-C films are not fused and are free to bond with atoms in the atmosphere, especially oxygen. With this surface adsorption of atmospheric oxygen, polarity increases because Si–O and C–O bonds are polar in nature. The greater difference in electronegativities between oxygen (\( \sim 3.5 \)) and silicon (\( \sim 1.8 \)) as compared to carbon (\( \sim 2.5 \)) implies that there is a higher affinity of oxygen with silicon. Therefore, there is an increase in the surface oxygen level when Si concentration is increased (as indicated in Fig. 5—XPS analysis without ion etching), hence resulting in greater polar component.

The dispersive component is directly related to the dispersive or induced dipole-to-dipole forces of the atoms in the films, and this force is governed by the following relationship:

\[
F \propto \frac{x}{r^3} \left[ \frac{1}{d} \left( \frac{1}{r^2} \right) \right],
\]

where \( x \) is the polarizability, and \( r \) the inter-atomic distance. It may be apparent that the dispersive component is affected by the surface roughness, but study has shown independency of wetting and surface morphology when the roughness is below 100 nm [21]. Since the roughest surface is 2nm, the dispersive component is very much related to the density of the film. The density is low at Si concentration below \( \sim 16.6 \text{ at} \% \) and increases as Si concentration increased.
concentration is increased as manifested by the deposition kinetics and bonding evolution [20]. The drop in density means an increase in the inter-atomic distance. Since the dispersive force is inversely proportional to the inter-atomic distance, the increase in the inter-atomic distance thus resulted in a decrease in the dispersive forces and ultimately the dispersive component of the surface energy (cf. Figs. 3 and 4 for Si below 16.6 at%). The increment of the dispersive component above Si atomic concentration of 16.6 at% is caused by an increase in density. In this case, more Si atoms bond with the sp\(^3\)-hybridized C atoms, hence turning them into sp\(^3\)-configured C–Si and/or C–C bondings. This will get rid of more of the longer bond length π-bonds (3.35 Å), thereby increasing the global density and result in a smaller inter-atomic distance as the Si concentration increases.

The number of adhered platelets is presented in Fig. 6. Result from ANOVA shows that Si concentration in a-C is indeed influence the number of adhering platelets. There is a decrease in the number of adhering platelets as the Si concentration in the film is increased. The decrement is comparable to Raman spectroscopy results, suggesting the increasing Si concentration and sp\(^3\)/sp\(^2\) ratio improves the haemocompatibility of the film. However, the evolution of the surface properties of these films does not directly affect the platelet count. There is a decrease in the total surface energy until the Si concentration of 16.6 at% is reached. The decrease in the platelet count with decreasing total surface energy in the low Si concentration region is also shown by Okpalugo et al. [11] on hydrogenated a-C films. The results of film with higher Si concentration cannot be compared, as there is currently no haemocompatibility study done on such a-C films, whether hydrogenated or not. In this case, there is an increase in the surface energy when Si concentration is increased further, and it is attributed by the increased in the polar component (as shown in Fig. 6).

The amount of adherent platelets and the activation on the film surfaces is inversely proportional to the ratio of albumin to fibrinogen adhesion on the surfaces [2,3]. While the adhesion of albumin (a water-soluble protein in the blood plasma) on the film can prevent the adhesion of platelets, fibrinogen is a protein that can enhance the adhesion and activation of platelets, and hence the thrombus when it is converted into fibrin by the action of the enzyme thrombin. The surface tensions of both albumin and fibrinogen are found to be similar at 65 mN/m [22], and the polar component of fibrinogen (40.3 mN/m) is higher than that of albumin (33.6 mN/m). From LW/acid–base approach, the polar component can be differentiated into base (electron donor) and acid (electron acceptor) components. It is found that the base components for all the films are very much larger than the acid component, indicating that the polar component of the surfaces is predominantly negatively charged. This is beneficial towards haemocompatibility as the platelets and proteins tend to have a net negative zeta potential of −8 to −13 mV [23]. Hence, there will not be any preferential adsorption of proteins and platelets due to electrostatic interaction. It is clear in Fig. 4 that the polar to dispersive component ratio increases as the Si concentration is increased. Therefore, the repulsion between the film surface and proteins increases as the Si concentration increases. Albumin is also repelled, but the effect is less intense than with fibrinogen due to its lower polar component. Furthermore, the dispersive component of all the films is relatively very much larger than the polar component; therefore, reflecting the interaction is predominantly based on dispersive forces. Since albumin has a higher dispersive component, it will have a more stable interaction with the film surfaces.

The discouragement of fibrinogen adsorption is evident from the evolution of platelet morphology. As shown in Fig. 7, the platelets on a-C film are mainly Types 3–5, and mainly Types 1–3 for platelets on a-C(Si37.6 at%) film. This shows that the doping of Si not only reduces the
number of adherent platelets but can also deter their activation. The undoped a-C film though causes a higher state of platelet activation, there is no evident of any aggregation. Unlike the coated Si wafer, the bare Si surface not only causes a higher number of adherent platelets and activation, but there are also numerous aggregation sites. This marks the initial stage of thrombus formation.

4. Conclusions

Undoped and Si-doped unhydrogenated a-C films have been synthesized by magnetron sputtering. Raman spectroscopy indicates that Si doping decreases the fraction of sp²-hybridized carbon bonding configuration. The total surface energy is lowest at Si concentration of ~16.6 at%. Below this concentration, the haemocompatibility improves due to the increase in sp³ fraction. Above this concentration, an increase in Si causes an increase in polar to dispersive component ratio. The negatively charged polar component can discourage preferred affinity of platelets and proteins; as a result, haemocompatibility is also improved at high Si concentration.

References


Fig. 7. SEM micrographs of the adherent platelets on (a) uncoated Si wafer, (b) undoped a-C film and (c) a-C(Si37.6 at%) film.


