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Kinetics and thermodynamics of human serum albumin adsorption on silicon doped diamond like carbon

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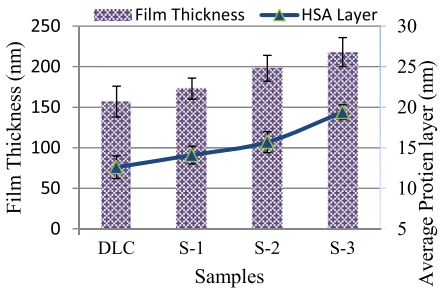
HIGHLIGHTS

- Diamond Like Carbon (DLC) and Silicon doped DLC were synthesised and characterised.
- Si-DLC increases the hydrophobicity and decreases the surface free energy.
- Adsorption study using human serum albumin (HSA).
- The adsorbed amount of HSA increases with increasing of Silicon content DLC.
- Adsorption process follow pseudo first order and Freundlich adsorption isotherm.

GRAPHICAL ABSTRACT



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ABSTRACT

To gain a better understanding of protein adsorption onto biomaterial surfaces is required for the control of biocompatibility and bioactivity. Various samples of diamond like carbon (DLC) and silicon-doped DLC were synthesised using plasma enhanced chemical vapour deposition (PECVD). The effects of surface morphology on the interaction of human serum albumin (HSA) with doped and undoped DLC films was investigated using spectroscopic ellipsometry (SE) and other surface analysis techniques. The results highlighted an increase in both contact angle and hydrophobicity with increasing silicon dopant levels. A reduction on the contact angle values.

After adsorption of HSA, the films showed a reduction in the contact angle with a significant change in the cosΔ and this gap increased with increasing surface coverage of HSA. The adsorption kinetics of HSA were also investigated and revealed that the maximum adsorption occurred at pH 5.0 and the process involved chemisorption. The experimental isotherm data were analysed using the Langmuir and Freundlich models. The amount of HSA adsorbed increased with contact time and reached saturation after 30 min. The adsorption process was found to be pseudo first order with respect to the bulk concentration and was dependent on both the concentration of protein and surface characteristics of the samples. The amount of adsorbed HSA was higher with higher levels of silicon doping of the DLC. Therefore, doping DLC may provide an approach to controlling the protein adsorption.

1. Introduction

Protein interaction is central to many biological processes including the interaction of cells with the surfaces of biomaterials.

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The adsorption of proteins on surfaces is an important fundamental problem involving interplay between electrostatic, van der Waals, steric and solvation interactions that result in very large competing energy scales and very long time scales. Furthermore, an understanding of protein adsorption is important in the biomedical field for drug delivery, biomaterials, extracorporeal therapy and solid-phase diagnostics [1].

The nature of the biomaterial and the protein affects the adsorption process. The chemical and physical properties of the surface such as the elemental composition, functional groups and surface energy are very important and play a role in enhancing or decreasing the adsorption of proteins or biological compounds of the implant.

Many different surface analytical techniques have been applied to study adsorption kinetics of proteins on a variety material [2–4]. Although the rates of adsorption of proteins on the surfaces are well known, the conformational changes occurring upon adsorption on the surfaces are not fully understood.

Diamond-like carbon (DLC) is an attractive biomaterial for coating human implantable devices [5,6], due to its unique combination of desirable properties including chemical inertness, high density, hemo-compatibility and low coefficient of friction [7]. Comparative studies showed that DLC has better biocompatibility and wear resistance than stainless steel, Poly-methyl mehtacrylate (PMMA) and cobalt chrome alloys [8–10]. Doping DLC with nitrogen, fluorine, titanium and silicon has been used to enhance the effectiveness of DLC as a biologically compatible coating [11–14].

Silicon doping has been reported to have a significant effect on the chemical stability of DLC [15]. Si-DLC overcomes some of the drawbacks mentioned, including low intrinsic compressive stress and mechanical resistance [16], which are beneficial for biomedical applications. It has previously been shown that the silicon incorporation can improve the adhesion between DLC films and their substrates [17,18], which indicates a good degree of biocompatibility for DLC coatings.

Improvements in blood compatibility with silicon doped DLC film where a decrease of inflammatory reactions was observed compared to undoped DLC [19].

The aim of this work is to investigate the adsorption of human serum albumin (*molecular weight ~66,550, isoelectric point PI ~4.7*) on doped and undoped DLC prepared by plasma enhanced chemical vapour deposition (PECVD).

2. Experimental

2.1. Film preparation and modification

Before deposition of the films, coupons of silicon 1.5 × 1.5 cm^2 were cleaned using ultrasound in acetone and isopropanol (1:1) for 5 min, followed by washing with distilled water, and then dried using nitrogen gas.

DLC and Si-DLC were deposited on the silicon by the radio frequency (RF) 13.56 MHz PECVD using a Diavac model 320PA (ACM Ltd.), with negative electrode self-bias voltages set at 400 V. The experimental equipment had been described in detail previously [4]. The cleaned substrates were placed in the deposition chamber on top of a water-cooled electrode driven by an RF power supply.

When the chamber pressure reached ~5 × 10^{-6} Torr, the glow discharge argon plasma (60 cm^3/min) was used to clean substrate and make the surface rough and to deposit evaporated coating material. In order to obtain a smooth, compact and uniform coating of DLC films [20], the deposition was performed under the following conditions: C_2H_2 was used as source gas, and argon (Ar) with tetramethylsilane (TMS) ($Si(CH_3)_4$ [%99.8 Sigma–Aldrich] were used as dopant gas. The (Ar:C_2H_2) flow ratio was fixed at (10:20) standard cubic centimetre (sccm), and the deposition time was fixed for 5 min. For Si-DLC, the various doping concentrations of silicon were achieved using different ratios of Ar:TMS to Ar:CH_2CH_2 were used. Detailed parameters are given in Table 1.

2.2. Surface characterisation

2.2.1. Spectroscopic ellipsometry

The dielectric constant and film thickness of DLC and Si-DLC films were investigated before and after exposure to HSA using a SOPRA GES-5E spectroscopic ellipsometery, in the photon energy range 1.25–7.75 eV with 0.05 eV steps. A system has been described in our previous work [12]. The laser wavelength (λ) was fixed at 532 nm, and the angle of incidence φ was set to 68.0°. A single beam of polarized light is incident on the surface and the polarization state of the light modified after reflection. This change in the polarization state is recorded in terms of the ellipsometric angles, Psi (Ψ) and delta (Δ) which are related to the optical and structural properties of the samples and defined by:

$$\tan \Psi \exp^{(i\Delta)} = R_p/R_s. \quad (1)$$

R_p and R_s are the complex Fresnel reflection coefficients of the parallel and perpendicular polarized light, respectively. The dielectric constant (ε) of the films can be obtained by the following equation:

$$\varepsilon = \sin^2\theta\left[1 + \tan^2\theta\left\{(1-p)^2/(1+p)^2\right\}\right] \quad (2)$$

where (θ) is angle of incidence and p is the complex reflectance ratio R_p/R_s [21]. The film thickness calculations were carried out using the installed (sopra) software. The silicon substrates were placed on the polar laser light to measure the basic thickness, followed the coated samples of DLC and Si-DLC before and after exposure to HSA; and then after the polar light parameters were obtained.

2.2.2. Contact angle and surface wettability

A goniometer KSV CAM 200 system was used to perform the contact angle (θ) measurements for samples before and after adsorption of HSA. The contact angle was processed by an image analysis system, which calculated both the left and right contact angles from the shape of the drop. Surface free energy of doped DLC was assessed by the Owens-Wendt-Rabel-Kaelble (OWRK) method using as testing liquids with known surface tension parameters such as: distilled water (H_2O), diiodomethane (C_2I_2) (from Sigma–Aldrich) and ethylene glycol $C_2H_4(OH)_2$ (from Sigma–Aldrich). The polar and dispersive components of the surface tension of the liquids were taken from the literature [22], the details are given in (Table 2). Drops of 5 μL of solvents were generated with a

Table 1
Process conditions for DLC and Si-DLC.

Parameters	Samples			
	DLC	S-1	S-2	S-3
rf. Power (Watt)	102	106	116	123
Pressure in Process × 10^{-2} (Torr)	0.77	0.91	1.28	1.71
TMS (sccm)	0	2	5	10
Film thickness (nm)	163 ± 16	170 ± 15	194 ± 14	213 ± 18

(rf): radio frequency, (W): watt, (TMS): Tetramethylsilane, (sccm): standard centimetre cube per minute, (nm): nanometre. Bias voltage: 400 V, deposition time: 5 min, Initial chamber pressure: ~5 × 10^{-6} Torr; argon to acetelene gas (10:20) sccm, Film thicknesses taken from spectroscopic ellipsometry (SE), (±) is SD for n = 7 samples.