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Characteristic of silver doped DLC films on surface properties and protein adsorption

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Abstract

Ag-incorporated diamond-like carbon (DLC) films were prepared on Si substrate using a hybrid deposition system composed of an end-Hall-type hydrocarbon ion gun and a silver DC magnetron sputter source. Ag was selected due to their potential values of biomaterial. The concentration of Ag in the films was varied from 0.1 to 9.7 at.% by controlling the fraction of Ar in the reaction gas mixture with benzene. In order to understand the influence of incorporated Ag on wettability, the surface energy and the protein adsorption as an indirect haemo-compatibility were measured. The surface energy of the Ag-incorporated DLC film decreased gradually with the increase of the Ag concentration. The haemo-compatibility was examined by the adsorption ratio of albumin/fibrinogen as an indirect method and improved with the increase of Ag concentration. The surface and biological behaviors of the films will be discussed in terms of the atomic bond characteristic and microstructure induced by Ag incorporation. Our results demonstrate that the Ag-incorporated DLC films are potentially useful as biomedical devices having good haemo-compatibility and hydrophobic characteristics.

Keywords: Diamond-like carbon (DLC); Protein adsorption; Surface energy; Wettability

1. Introduction

Diamond-like carbon films have been a good candidate for some application such as blood contacting devices [1,2] and cells contacting materials [3] due to their excellent mechanical properties such as low coefficient of friction [4], wear resistance properties [5], extreme good chemical inertness and biocompatibility [6,7]. Therefore DLC films have been of interest as a protective coating in medical implants such as a replacement for hip [8], knee [9], coronary artery stents [10] and mechanical heart valves [11]. However, the biological behavior of the implant is strongly influenced by the chemical properties at the interface. For example, whenever a foreign surface of biomaterial is placed in contact with blood, the protein in blood first adsorbs to the foreign materials, resulting in the adhesion and activation of subsequent platelet. These induce the coagulation of blood when the activated platelets produce enzymatically activated substances. Consequently, the protein adsorption is the crucial event as a first process of haemo-compatibility between blood and the biomaterials because it influences the subsequent fabrication of thrombus [12]. Therefore, it is very important to control the surface chemistry of an implant, particularly the composition, to produce a specific surface with a well-defined biological reaction. In this point of view, doped DLC films have attracted much attention recently. Several different research groups investigated the change of surface properties of DLC films by adding a third element such as Al [13], Ni, Fe and Si [14]. It is well known that all of these properties can be changed within a certain range by the addition of other elements into the DLC. For example, H. Schulz et al.

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reported that the addition of Al into DLC film decreases surface energy while contact angle increases from 70 to 98° [13] and J. S. Chen et al. showed an increase of the contact angle by the addition of Al and Fe into DLC film while a decrease of the contact angle by the addition of Ni [14]. At the same time, doping of Ag into DLC films is also potentially valuable as biomaterials. Ag has been reported as a powerful antibacterial agent that has been used in biomedical engineering with good effects [15–17]. Because Ag as a cytotoxic element, can be used in applications where no bacteria or cells should attach to a surface, such as temporary implants and surfaces of medical devices that inhibit cell proliferation and differentiation are required. However, doping of Ag into DLC film can make the change of wetting angle and surface energy and it can also affect the haemo-compatibility even though there are some contradictive results on the haemo-compatibility with wetting angle [18–21]. For example, F. Z. Cui et al. reported that the hydrophilic surfaces suppress the protein adsorption as well as platelet adhesion [18] and M. I. Jones et al. reported that the hydrophobic surface is better than the hydrophilic surface for coating on medical guide wire and protein absorption, platelet attachment and activation for cardiovascular applications [1]. It is unclear which property is more preferable. Thus, the haemo-compatibility of Ag-incorporated DLC films should be investigated with their composition, wetting angle, surface energy or atomic bonding structure together due to bio reaction to surface influenced by various factors, including surface energy, surface compositions and atomic bonding structure. In our work, we studied the characteristic of Ag doped DLC films on the surface properties and protein adsorption with detailed understanding of the composition, surface energy and structural effects.

2. Experimental

A schematic diagram of the hybrid deposition system used in our work is shown in Fig. 1. The deposition system composed of ion-beam deposition of benzene and magnetron sputtering of silver. The benzene was introduced into the end-Hall-type ion gun to obtain the hydrocarbon ions. Typical values of anode voltage and current are 90 V and 0.32 A, respectively. Argon sputtering gas was supplied to the sputter gun equipped with Ag target of a high purity (99.99%) with a diameter of 5 cm. Typical DC power supplied to the sputter gun was about 298 W (620 V, 0.48 A). The total gas flow used for Ag-incorporated DLC film was 18 sccm for all the samples and the fraction of Ar in the reaction gas was varied from 0.85 to 0.93 (15.3 to 17.7 sccm) to control the Ag concentration in the deposited films. The base pressure in the reactor was $<2\times10^{-5}$ Pa, whereas the deposition pressure varied in the range of 0.08–0.15 Pa, depending on the fraction of Ar gas. Before deposition, the substrate was cleaned using the Ar ion beam with a pressure of 0.10 Pa and a bias voltage of −400 V for 30 min. And then, the buffer layer of DLC film was deposited for 8 min at a bias voltage of −800 V with an open shutter condition. The thickness of the buffer layer was 52±3 nm. Subsequently, the Ag-incorporated DLC film with 150±20 nm was deposited for 10 min at a bias voltage of −200 V. Pure DLC films were also prepared using only the hydrocarbon ion beam at a negative bias voltage of −200 V without operating the sputter gun. The deposition time was adjusted to obtain the thickness of 200±15 nm for all the samples. A p-type Si (100) wafer with thickness of 500±10 μm was used for the substrate, and this was placed on a rotating substrate holder placed about 22 cm from the ion gun. A thin Si (100) wafer of thickness 100±2 μm was also used to calculate

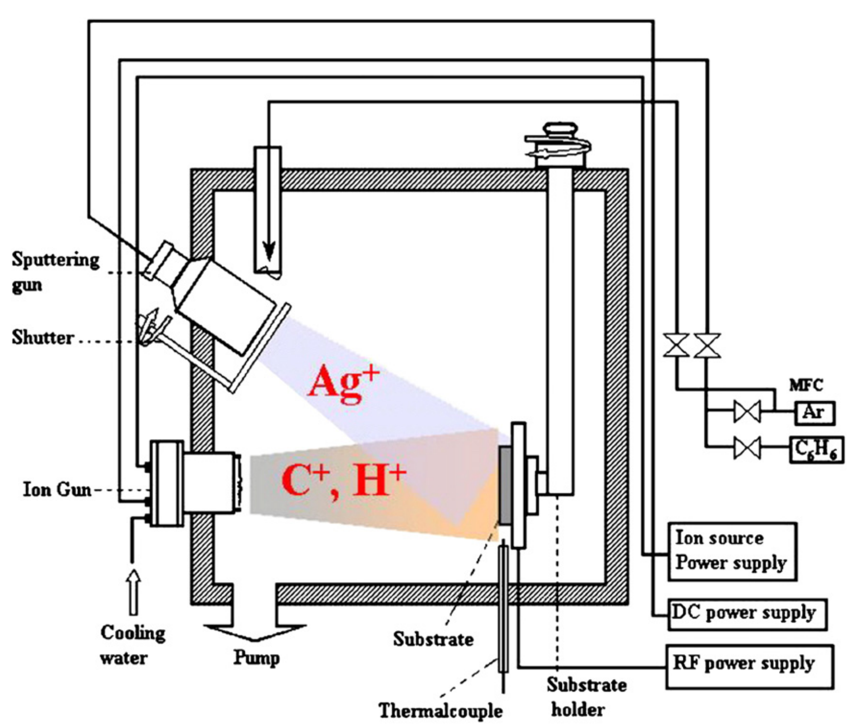

Fig. 1. A schematic diagram of hybrid ion-beam deposition system.