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Biological activity of silver-doped DLC films

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ABSTRACT

The technique of combined DC metal arc and carbon pulsed arc was used to deposit thin solid films containing up to 6.5 at.% of silver. The microstructure and antibacterial properties of silver-doped diamond-like carbon (DLC) films have been investigated. Silver nanoparticle of flat disk shape located inside of an amorphous carbon matrix revealed excellent antibacterial properties concerning *Staphylococcus aureus* bacteria. Titanium substrates with DLC films doped with silver have an inhibiting effect on growth of some tumors, in particular, on rat neoplastic C6 glioma. This result is new and opens further possibility for application of DLC:Ag composite in medicine.

1. Introduction

Progress in development of plasma deposition technique has enabled obtaining unique high-quality synthetic material that exists in the form of solid thin film such as diamond-like carbon (DLC) and outlined field of its application. Nowadays the material is effectively used for enhancing the lifespan of hard-metal cutting tools [1], automotive parts [2], moulds and dies [3]. DLC films are widely used in optical and magnetic industry as protective coatings for digital storage devices [4]. In addition to superior mechanical properties of these materials recent studies also revealed good biocompatibility that is demonstrated by decrease of platelet adsorption activity for implants used in vascular and cardio-surgery [5], absence of inflammatory reactions in body cells [6], and prevention of bone osteolysis for large implant devices such as artificial hip and knee joints [7]. DLC films doped with silver [8], platinum [9] or copper [10] greatly increase their antibacterial properties. But only the first steps have been undertaken in this direction and there is not enough clarity in comprehension of optimal structure of a carbon-metal DLC composite coating and its interaction with bone und tissue cell as well as with neoplasm cell. The work discusses both antibacterial properties and influence of silver-doped diamond-like carbon (DLC:Ag) films on growth of some tumor cells.

2. Experimental methods

The DLC films were obtained by vacuum pulsed-arc deposition described in detail elsewhere [11]. The technique does not allow use of either substrate heating or bias voltage due to high energetic plasma supplied by the Hall type plasma source. The latter was operated in such a mode as to provide carbon ion energy ranging from 60 to 80 eV that is optimal for obtaining DLC films with high content of four-folded carbon bonds [12]. Silver was introduced in these films by DC arc burning on the silver cathode. The layered method of carbon and silver deposition was used to obtain DLC:Ag composite films. Polished strips made of the Ti–1.6Al–5Mo–4V titanium alloy, silicon wafers and sodium chloride monocrystals were used as substrates for investigating the biological properties, chemical composition and structural properties of these films, respectively. The elemental composition was examined by dispersive X-ray micro analysis (Philips SEN-15 scanning electron microscope equipped with Genius 2000 X-ray micro analyzer). The film microstructure was determined by transmission electron microscopy (JEM-200CX). Chemical structure was characterized by Raman (argon laser, $\lambda = 514.5$ nm) and X-ray photoelectron spectroscopy, XPS (ES-2400). Philips SEN-15 scanning electron microscope was used to investigate bacterial activity of DLC:Ag films. Technique of sample preparation for biological researches is described in Section 3.2.

3. Results and discussion

3.1. Film characterization

It is well-known that DLC film quality is largely determined by methods and conditions of their producing. The highest amount of sp^3 bonds in carbon film can be achieved in the case of using a laser or arc technique for their deposition [13]. The quantity for four-folded σ-bonds in DLC films is very important for both their mechanical properties and wettability [14] as well as for platelets adsorption [5]. As a rule the more sp^3/sp^2 ratio is the better biocompatible properties

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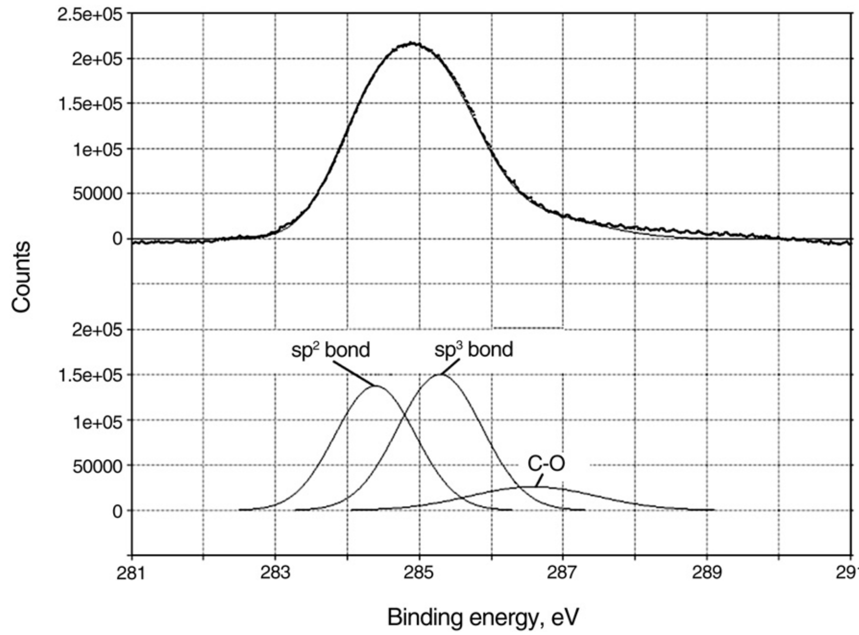

Fig. 1. C1s XPS spectrum of the DLC film prepared by the pulsed arc.

of DLC films. Thus, it is necessary to choose a deposition method that would provide as many sp^3 bonds as possible in composite DLC:Ag films because sp^3 bonds content is decreased by silver dopant [6].

The XPS spectrum of the core C1 level is shown in Fig. 1. The spectrum is deconvoluted in the peaks placed at binding energies of 284.4, 285.3, and 288.6 eV corresponding to sp^2, sp^3, and C–O bond, respectively [15]. The content of sp^2 and sp^3 bonds in this DLC film is about 47.4 and 44.3%, respectively. The oxygen presence on the film surface mainly leads to the formation of C–O bonds in quantity of 8.3%. If we take into account that when performing XPS analysis a film depth does not exceed a few nanometers and an upper layer of a DLC film is rich in graphite-like phase [16] then an actual ratio of sp^3/sp^2 in the film is higher in comparison with that determined by the XSP method. This suggestion is confirmed by the Raman investigations.

Fig. 2 shows the Raman spectra of the DLC film deposited on a silicon substrate at the discharge voltage of 300 V and capacitor bank capacity of 2400 μF. The spectral curve has high symmetry. Its deconvolution in D-peak located at 1376.9 cm^{-1} and G-peak located at 1565.4 cm^{-1} makes it possible to estimate the quality of DLC films. One can see the very low D-peak intensity, I_D, in comparison with G-peak intensity, I_G. The I_D/I_G ratio is 0.12. This parameter value is indicative of high content of diamond-type bonds in the DLC films not less than 85% [17].

The silver content in DLC films was examined by X-ray micro-analysis. Two series of DLC samples with silver percentage of 3.5 and 6.5 at.% were used in the biological experiments. In addition to carbon and silver the DLC films contain about 2 at.% of oxygen that is less than that defined by XPS analysis. This mater is evidence of chemical adsorption of oxygen on the film surface during contact with air. Transmission electron patterns taken in bright mode give a silver structure as nanoparticles embedded into carbon matrix.

The silver particle pattern is in sharp contrast because the resulting contrast for Ag is 50 times higher in comparison with C. In the case of low silver amount, there is an ensemble of disk-shaped particles disposed randomly in a DLC film (Fig. 3) as opposed to silver nanoparticles self-assembled into arrays observed in [9]. The particle

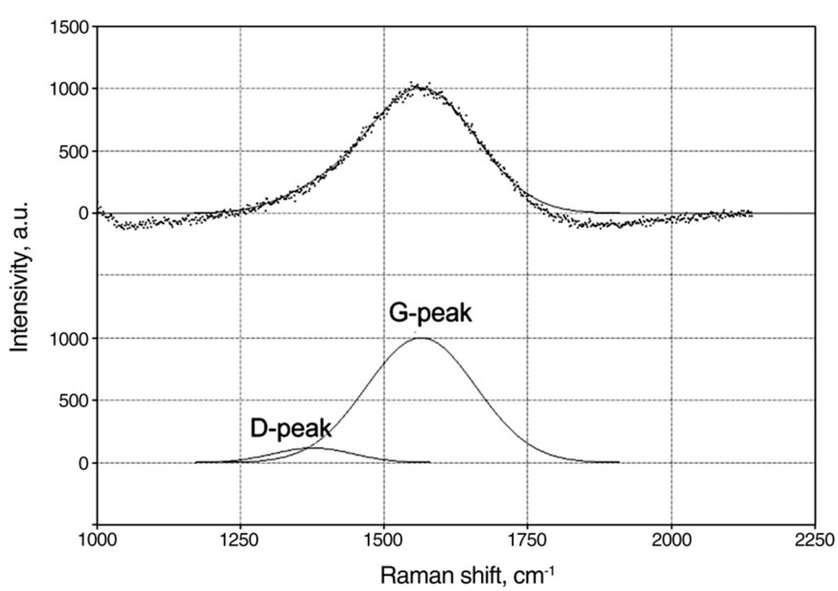

Fig. 2. Raman spectrum of the DLC film prepared by the pulsed arc at main discharge voltage of 300 V.