Vacuum 110 (2014) 78–86

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Silver implanted diamond-like carbon coatings

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ARTICLE INFO

Article history:
Received 14 May 2014
Received in revised form
3 September 2014
Accepted 4 September 2014
Available online 16 September 2014

Keywords:
Diamond-like carbon
Silver
Implantation
CVD
PVD

ABSTRACT

Modern technologies in surface engineering allow for the creation of new and modification of existing types of coatings, thereby improving their performance, and often adding extra features, such as antibacterial properties. In presented work a possibility of application of ion implantation method for the modification of the physicochemical properties of carbon coatings is presented. Gradient a-C:H/Ti coatings were subsequently implanted with two doses of silver ions: 7 and 10 $\times$ 10^{16} ion/cm^2, respectively. Physicochemical characteristics like chemical structure and composition, morphology, surface topography, surface free energy, hardness and adhesion were determined. Silver depth concentration profiles measured using AES show correlation between applied dose and surface chemical composition. Optimal depth distribution of silver was observed for both values of Ag^+ doses. Implantation of silver in the DLC coating smoothens the surface, changes the I_D/I_G ratio and affects the surface free energy by changing both values of polar and dispersive component. Part of it may be also related to the possible hydrogen release occurring during the implantation. Mechanical properties of silver implanted carbon coatings were slightly lower, without noticeable differences between both Ag^+ doses. Ion implantation technique appears to be an effective way for surface modification and tailoring the properties of carbon coatings.

1. Introduction

Growing number of reports related to allergy issues of patients with medical implants creates the need of a development of new biocompatible biomaterials. New materials with controlled bioactivity and other useful properties that can improve the quality of life and the healing processes of patients suffering from various types of allergies are of special interest [1,2]. In this regard diamond-like carbon (DLC) coatings due to their very special physicochemical [3–6] and mechanical [6–11] properties combined with good biocompatibility [11,12] and bactericidal activity [13,14] have been considered as a good candidate for variety of biomedical applications [8,15,16]. Although the techniques of the deposition of DLC coatings are well known and described elsewhere the intensive studies on the synthesis and modification of carbon coatings which prove their high application potential are still conducted. One of these focuses on the enhanced bactericidal activity. For that purpose silver seems to be a perfect candidate. It is known to be an antibacterial agent with a very broad spectrum of activity and has a long history of application in medicine [17,18]. Therefore, over the past few years a growing interest in evaluation of modern and hybrid techniques for the synthesis of variety of silver incorporated DLC coatings is seen. Marciano et al. [19] produced silver incorporated diamond-like carbon coatings using Plasma Assisted Chemical Vapour Deposition (PACVD) method. Silver nanoparticles were introduced to the coating by spraying its water solution obtained by electrodeposition method. After silver deposition, another DLC thin interlayer (~25 nm) was synthesized to fix the silver nanoparticles. Raman spectra showed that the phase composition of obtained coatings was not affected significantly due to the incorporation of silver. It was also shown that silver nanoparticles cannot chemically bind with carbon, but must be captured by another top DLC layer. In work [20] RF reactive magnetron sputtering technique was applied to synthesize Ag doped DLC coatings. Obtained silver concentrations varied between 1 and 12 at.%. Authors reported significant changes in the chemical structure of obtained coatings, especially increasing intensity of the sp^2 and decreasing intensity of the sp^3 hybridized carbon, as well as

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http://dx.doi.org/10.1016/j.vacuum.2014.09.001
0042-207X/

Table 1
Chemical composition of AISI 316L (%wt.).

Element	C	Si	Mn	P	S	Cr	Ni	Mo	Fe
AISI 316LVM	Max. 0.022	Max. 0.583	Max. 1.669	Max. 0.021	Max. 0.022	16.48	13.38	2.49	Rest

the overall increase in the sp^2/sp^3 ratio. Pulsed filtered cathodic vacuum arc deposition system was applied by Kwok et al. [21] for the synthesis of silver incorporated diamond-like carbon coatings using Ag–C co-axial target. Authors obtained rather high concentrations of silver in carbon coatings. Changes in chemical structure of obtained samples, particularly sp^3/sp^2 ratio, were in authors' opinion rather attributed to negative sample bias than to the silver atomic concentration. The contact angle value for water varied between 71° for the highest silver concentration through 79° for the medium and finally 67° for the lowest Ag concentration, however also here the strong influence of negative bias on the amount of sp^3 hybridized carbon should be considered. Choi and co-workers [22,23] proposed carbon coatings deposited with use of the end-Hall-type hydrocarbon ion gun (using benzene) simultaneously doped with silver by means of DC magnetron sputtering technique. The concentration of silver varied between 0.1 and 9.7 at.%. It was shown that the total surface free energy of Ag-doped DLC films is reduced with silver concentration increase. Authors also observed an increase of the graphite-like bonds in amorphous carbon matrix with increased concentration of silver. In our recent work [24] we elaborated similar hybrid deposition technique. It combines carbon coating, synthesized with use of RF PACVD method, at the same time doped with silver delivered via pulsed magnetron sputtering technique. The obtained results showed that doping of the DLC coatings with silver by magnetron sputtering process lowers the hardness and increases the surface development parameter RL_0. In works [25,26] authors proposed plasma immersion ion implantation (PIII) as a deposition method of Ag-doped DLC gradient nanocomposite coatings. The study showed that Ag-doping has a slight effect on carbon hybridization and disordering while having smoothing effect on the surface topography. What was interesting, authors also reported that silver doping increases the strength of hydrogen-free DLC films and simultaneously decreases the strength of hydrogenated DLC films.

There were three common conclusions that were reported in majority of cited papers. Authors of works [21–25] unanimously reported that silver atoms incorporated into amorphous carbon matrix occur mostly in the metallic state, thus they do not form any chemical bonds with carbon. Usually, the authors have not found significant changes in mechanical performance of the coatings. At the same time a decrease of residual stress accompanied with slightly lower hardness of the coatings was noticed [19,23–25].

Despite wide range of technologies used for the synthesis of silver doped diamond-like carbon coatings there is lack of information on the use of ion implantation method to modify the preformed carbon coating with silver. Similar technique was reported in Ref. [27], however in that work silver ions were implanted to substrates made of pyrolytic carbon, mostly used in cardiac surgery applications. Therefore authors of this work propose some new complex surface modification utilizing highly biocompatible diamond-like carbon coatings subsequently implanted with silver ions. Two doses of silver ions were implanted into hydrogenated DLC layers and their basic physicochemical characteristics was performed. The results show that proposed method of modification, even though complicated and expensive, provides ample possibilities of selective surface modification of materials for variety of applications with special regard to those requiring the antibacterial activity (foreseen in our further studies).

2. Materials and methods

Studied samples were made of AISI316LVM austenitic steel (confirmed by the X-ray fluorescence spectroscopy - SRS 303 Siemens, see Table 1). Mirror polished flat discs of 16 mm in diameter and 6 mm thick were used. Before the modification samples were cleaned in methanol bath in ultrasonic cleaner for 10 min and then dried using compressed air.

Carbon coatings for the ion implantation processes were synthesized with use of the *Radio Frequency Plasma Assisted Chemical Vapour Deposition/Magnetron Sputtering* (RF PCVD/MS) system described in Refs. [5,28]. A proper adhesion of DLC coatings was ensured by the application of gradient Ti–Ti_xC_y–DLC interlayer with a thickness of ca. 200 nm. Synthesized carbon coatings, with the thickness of 700 nm, were subsequently implanted with Ag^+ ions using a 70 kV ion implanter described in Ref. [29]. The implantation processes were carried out with the use of silver ions with energy of 15 keV. In order to determine the influence of silver ion implantation process onto overall physicochemical properties of carbon coatings two ion doses of 7 and 10 × 10^{16} Ag^+/cm^2 were applied (denoted from here as DLC/Ag1, DLC/Ag2 respectively). The individual doses of ions were selected in such a way as to obtain coatings with silver concentration equal to 2 and 4 at.% respectively, assuming a uniform distribution through the film. A beam of ions, prior to the implantation process was filtered using the magnetic separator (to avoid multiply charged Ag ions) and additional masks were used to give it the final dimensions of 10 × 70 mm. The Ag^+ flux density for each dose was adjusted separately, so as to avoid excessive heating of the sample during the process, and was less than few $\mu A/cm^2$ (as measured with use of the Faraday cage mounted below the sample holder). In addition, to obtain the uniform distribution of silver, the sample holder was oscillating. The silver implantation profile was also simulated with use of SRIM

Table 2
Parameters of the synthesis process.

Phase	Plasma etching	Pulsed magnetron sputtering	DLC deposition	Ion implantation
Details	Pressure: 2 Pa Time: 10 min RF bias: −800 V Ar flow: 15 sccm Temp.: <200 °C	Pressure: 0.5 Pa Time: 12 min RF bias: −300 V Power: 2.2–2.7 kW Ar flow: 9 sccm CH_4 flow: 1–7 sccm Temp.: <200 °C	Pressure: 20 Pa Time: 50 min RF bias: −300 V Precursor: CH_4 Temp.: <200 °C	Pressure: 1 × 10^{-5} Pa Energy: 15 keV Dose: 7 × 10^{16} Ag^+/cm^2 10 × 10^{16} Ag^+/cm^2 Temp.: 25 °C