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Structure and properties of silver-containing a-C(H) films deposited by plasma immersion ion implantation

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Abstract

In this study, we have grown silver-containing hydrogenated (a-C:H) and non-hydrogenated (a-C) amorphous carbon coatings by two plasma immersion ion implantation methods: I) chemical vapor deposition of methane combined with pulsed filtered cathodic arc deposition of silver, and II) by alternating arc pulses from graphite and silver in a dual cathodic arc plasma source. This unique "bias selective" feature of the deposition system allowed the deposition of silver with the substrates at ground and avoided the sputtering of the grown a-C film. Chemical composition of the samples was analyzed by acquiring their compositional depth-profiles using radio-frequency Glow Discharge Optical Emission Spectroscopy (rf-GDOES), while the microstructural properties were analyzed by X-ray absorption near edge spectroscopy (XANES) and Raman spectroscopy. In this contribution, we compare mechanical and biomedical properties by means of nanoindentation and cell viability tests, respectively, of a-C(H) films obtained by two different plasma immersion ion implantation techniques.

Keywords: Plasma immersion ion implantation; Amorphous carbon; Silver; X-ray absorption spectroscopy; Raman; Nanoindentation; Cell viability

1. Introduction

Diamond-like carbon (DLC) films are of interest to many applications due to their favorable mechanical and tribological properties [1–4]. They have also generated interest in the biomedical field because of their high biocompatibility and perform well as a surface that will support appropriate cellular activity, [5–13]. Strictly speaking, the term "DLC" includes a broad range of sp^3-rich carbon materials with good tribological properties. In this manuscript, we will use the common notation of a-C:H and a-C to refer to hydrogenated and hydrogen-free DLC deposited by two different plasma immersion implantation and deposition techniques, respectively. Because of their amorphous nature, amorphous carbon films are capable of embedding metallic elements, which can add to their functionality. In recent work, the biocide function of radio-frequency plasma-assisted chemical vapor deposition (RF-PACVD) a-C:H films has been described as they were doped with certain toxic elements such as silver, copper and vanadium deposited using DC (direct current) magnetron sputtering [14], Other studies have pointed out the possibility of incorporating silver into a-C coatings by pulsed laser deposition (PLD) with the use of a silver–graphite composite target [15,16]. In general, the underlying idea of these studies is that by varying the alloy element concentration, it is possible to tailor the composite metal–DLC film to a desired point where the biocidal effect of the metal against microorganisms such as harmful bacteria is maximized yet the biocompatibility is not (yet) jeopardized. Other studies in the deposition of mixed DLC–Ag materials have been carried out by magnetron sputtering combined

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with pulsed laser deposition [17], electron cyclotron resonance DC (ECR-DC) sputtering [18] and thermionic vacuum arc [19].

Composite amorphous carbon/Ag films have also attracted attention with respect to their optical properties, these coatings can be made transparent and have low emissivity which make them attractive for window applications [20].

It has also been suggested that the doping of DLC with conductive metals such as silver may be used as coating materials for electrodes in electrochemical analysis in microelectromechanical systems (MEMS), doped DLC materials may provide a window for a broad range of electrochemical reactions [21].

Independently of the deposition technique of choice, silver and carbon films have contrasting nucleation modes. In a-C or a-C:H films grown by plasma immersion ion implantation and deposition (PIIID), the growth occurs in the sub-surface with energetic ions facilitating the insertion below the surface, and thereby forcing the carbon ions to be closer packed, promoting the formation of sp^3 bonds. On the other hand, silver is known to have a three dimensional (3D) growth, and the minimum thickness for coalescence can strongly depend on the contacting substrate properties [22]. Density functional calculations of the interaction energies of silver adatoms on a graphitic carbon surface have indicated that carbon atoms could be hybridized with silver atoms. Scanning tunneling microscopy (STM) images of silver dimers confirmed this, as images would appear as two distinct atoms on the graphite surface and not as a blurred image of the two [23]. In a-C:H materials, there is the possibility that all dangling bonds of carbon are saturated with hydrogen, and any possible interaction between silver and carbon is consequently minimized. Detailed analysis of the nanostructure of pulsed laser deposited a-C/Ag by use of Z-contrast transmission electron microscopy (Z-TEM) has been reported in a similar study [15]. Such nanostructure was described as arrays of nanocrystalline silver particles embedded in an amorphous carbon matrix with formation of silver clusters as small as 5 nm.

Since clustering during deposition can be one difficulty in the deposition of amorphous carbon–Ag films, processes far from thermodynamic equilibrium, such as PLD [24] and PIIID [25] are in fact good deposition choices of non-hydrogenated a-C–Ag at room temperatures. In contrast, other techniques, which involve higher film condensation temperatures such as RF-PACVD, can result in the loss of a homogeneous nanocomposite profile due to segregation of the metal (silver) to the surface.

In the present work, we have made an exploratory study of the mechanical and biomedical properties of nanocomposite a-C:H–Ag and a-C–Ag coatings prepared using two different hybrid deposition techniques: i) Ag cathodic arc in reactive methane (CH_4) atmosphere and ii) dual-cathode pulsed cathodic arc (PCA) deposition using silver and graphite cathodes. The first of these techniques is a hybrid chemical and physical vapor deposition (CVD/PVD) technique, whereas the latter is a special form of PVD technique.

2. Experimental

Films of a-C:H–Ag and a-C–Ag have been deposited using the dual-cathode arc deposition system shown in Fig. 1. The system contains a dual-cathode "triggerless" mini-gun, which was designed to operate in pulsed mode [26,27]. The two cathodes incorporated in the source were graphite (C1) and silver (C2). The pulsed operation of these cathodes was controlled using a custom National Instruments' LabView™ software. Once the computer has sent a signal to the arc power supply, pulsed arc discharges on individual cathodes are triggered simply by application of a high open circuit voltage (typically 600 V). The plasma stream produced by the source is injected into a 90-degree filter to remove most of the macroparticles, which were formed during the cathodic arc process.

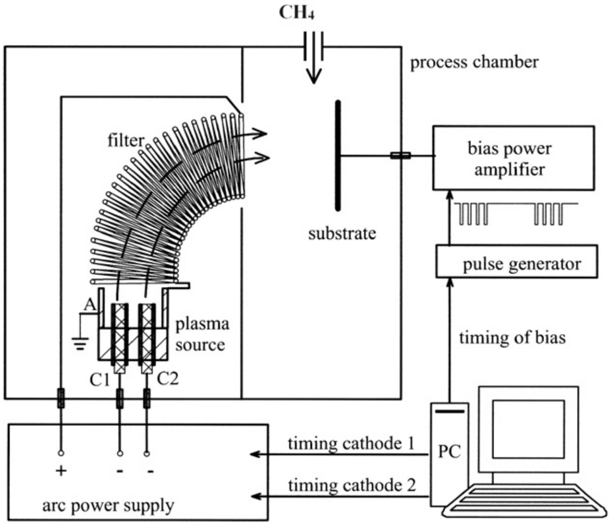

Fig. 1. Schematic of species-selective bias plasma immersion implantation and deposition chamber. The system synchronizes pulsed plasma produced by a dual-cathode "triggerless" mini-gun with pulsed biasing of the substrates. The system is also equipped with a gas inlet port with mass flow controller, which allows for the controlled supply of methane into the chamber.

For the deposition of a-C:H–Ag, carbon and hydrogen are taken from the process gas and silver came from the arc cathode. In the system, the substrates were biased with 1 kV pulses that were 2 μs long, with a duty cycle of 12.5%. Pulsed arcing from the silver cathode occurred simultaneously with the plasma immersion ion implantation and deposition of ions from the methane plasma.

For the deposition of a-C–Ag, the feedstock materials were exclusively the two cathodes; no background gas was needed or added. The residual gas pressure was typically in the 10^{-4} Pa range. One of the advanced features of the system shown in Fig. 1 is that it is equipped with a computer-controlled bias amplifier that can synchronize substrate bias with the pulsed production of plasma. Thus, in order to avoid excessive re-sputtering of carbon atoms during the deposition of the silver, no bias voltage was applied during the deposition of the metallic component, while bias was present when carbon ions arrived [27].

Pure hydrogenated DLC films were initially deposited by CH_4 plasma immersion ion implantation and deposition. In this case, the system was operated in a continuously pulsed bias mode. Methane was supplied into the chamber at a flow rate of 30 sccm. The working pressure was about 9.3 Pa (70 mTorr). Similarly, the silver-containing amorphous hydrogenated film (#2) was