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Phase transformation of diamond-like carbon/silver composite films by sputtering deposition

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Abstract

This study fabricated hydrogenated diamond-like carbon/silver bioceramic films on glass substrates using radio frequency magnetron sputtering with a single silver target in an atmosphere of Ar/CH4 mixture. The effects of applied power on the composition and microstructure of bioceramic film were evaluated. A phase transformation, amorphous diamond-like carbon → nano-silver precipitation → nano-silver growth in the amorphous diamond-like carbon matrix was observed during sputtering. The film growth rate, surface roughness, silver content and size of silver nanoclusters in the films all increased with the silver target power due to the higher flux of sputtered silver species toward the substrate.

Keywords: B. Nanocomposites; Silver-containing diamond-like carbon; Sputtering

1. Introduction

Metastable amorphous carbon film exhibits a great variety of bonding structure and accordingly electrical, optical, chemical and mechanical properties [1,2]. By adjusting their microstructures and hybridizations, carbon films with various properties can be used in many applications, such as protective, heat-conducting, hydrophobic, biocompatible and other functional surface treatments on workpieces [3–6]. Most of the studies used low-temperature techniques to coat the amorphous hydrogenated carbon (a-C:H) films utilizing the plasma enhancement such as plasma enhanced chemical vapor deposition (PECVD) [7,8], ion beam deposition [9], magnetron sputtering [10,11], and vacuum arc deposition [12–15]. Generating plasma effectively decomposes and ionizes the hydrocarbon gas to synthesize a carbon film on substrate surface. Among these deposition techniques, magnetron sputtering and vacuum arc deposition are two mostly chosen processes because of their low cost, simplicity and competent deposition rate. However, the high residual stress accumulates with increasing film thickness, which causes the detachment of diamond-like carbon film from substrate [15–18]. It has been reported that the residual stress in diamond-like carbon (DLC) films can be reduced by doping metal elements or carbides [19–23]. Doping metal elements in a-C:H films do not only prevents the film detachment and improves the electric conductivity but also enables new antimicrobial functions to a-C:H films [23–25].

Many heavy metal elements have been found with antimicrobial ability [26]. Such antibacterial effect of metal

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ions is long term and environment resistant, especially that of the silver nanoparticles. Not only their effectiveness against multiple drug-resistant bacteria by hindering respiration and division of bacteria, but also their limited toxicities to mammalian cells have been demonstrated [27,28]. It is generally reported that metal ions binding to thiol groups in enzymes and proteins play an essential role in antimicrobial action. In addition, metals deposited on cell membranes or cell walls can inhibit cell division and disrupt membrane integration [28,29].

The aim of the present work is to establish a reactive radio frequency (RF) magnetron sputtering process with single silver target to deposit silver-containing a-C:H films under an argon–methane mixture atmosphere. There are two ways to alter the contents of silver in the films: adjusting the mixture ratio of argon and methane at a constant target power, or adjusting the target power input under a constant argon–methane mixture atmosphere. Since adjusting the target power takes lesser process time and is more convenient for setting sequences in industrial processing, we chose the latter way in this study. The correlations between the target power and the structure of the synthesized films were investigated to evaluate the applicability of these films for potential usages.

2. Materials and methods

Glass substrates with a size of 1 cm in diameter and 2 mm in thickness were cleaned in an ultrasonic bath with the sequence of acetone followed ethanol for 15 min each. After air drying, the substrates were loaded into the deposition chamber. The reactive sputtering technique utilized in this study combines magnetron sputtering and RF plasma-enhanced chemical vapor deposition. The generated plasma species between sputtering gun and substrate simultaneously sputters the atoms of silver target material and decomposes the CH_4 gas as the carbon source for synthesizing the composite films. The setup of equipment and the detailed deposition procedures have been described in previous works [30,31]. The distance between silver target and substrates was fixed at 60 mm. After evacuating the chamber and heating the substrates to 200 °C, the methane–argon gas mixture in a ratio of 1/1.5 was introduced and the RF plasma was triggered. The deposition parameters are listed in Table 1.

The surface and cross-sectional morphologies of the deposited films were observed using a scanning electron microscope (SEM, JSM-6500) and an atomic force microscope (AFM, NanoMan NS4+D3100). The compositions of deposited films were analyzed using an energy dispersive X-ray spectrometer (EDX) attached on the scanning electron microscope. Since the hydrogen content in films cannot be analyzed by EDX, the ratio of measured Ag to C was used to represent the silver content in films. The crystallographic structures of films were characterized by grazing incidence X-ray diffraction (GIXRD, SIEMENS D5000), with a Cu Kα radiation source. A Raman spectrometer (BWTEK-MiniRam^{TM}II) was used to analyze the bonding of a-C:H phases in films. High-resolution transmission electron microscopy (HRTEM, PHILIPS F-20) was used to identify the structure of deposited film.

Table 1
Reactive sputtering deposition conditions for Ag/a-C:H films in this study.

Items	Parameters and values
Target material	Silver (purity 4 N, ψ7.62 cm)
Target power (W)	100, 150, 200, 250, 300
Substrate temperature (°C)	200
Gas flow ratio (Ar/CH_4)	1/1.5
Working pressure (Pa)	0.23
Deposition time (min)	25

3. Results and discussion

Fig. 1 shows the growth rate and Ag/C ratio of the films obtained at different target powers. With increase in the target power, the plasma density and accompanied ion bombardment on silver target intensify the flux of ejected silver species, which causes increased film growth rate and Ag/C ratio. The Ag/C ratio increases exponentially with target power, but the increase of film growth rate is not regular. Such nonlinear film growth rates induced by the target poisoning effect and electron–gas interactions of reactive gas molecules are commonly seen in an RF reactive sputtering process. For the films obtained at below 200 W target power, the fraction of silver in the films is minor, which indicates that the film growth rate at lower target power is mainly contributed by the deposition of the a-C:H matrix. The low fraction of silver can be attributed to the limited sputter yield of silver atoms with lower kinetic energy of incident ions and the formation of carbide on target surface (target poisoning). Large input energy is consumed by the complex interactions between hydrocarbon molecules and electrons, produceing various species which affect both the formation of carbide on silver target and films on formation. This causes irregularity of the film growth rate. Once the target power reaches 300 W, the emission rate and kinetic energy of ions are sufficient to remove the carbide on the target; the flux of silver suddenly increases and dominates the film growth rate.

The irregular dependence of intensity ratio, I_D/I_G, in Fig. 2 which was calculated from Raman spectra, also implies that these various bonds in films were caused by such complex plasma interactions. The I_D/I_G, an index of the disorder degree of a-C:H phase, initially decreases with the silver content, then rises to a maximum at 200 W, and subsequently decreases again. It disagrees with the typical trend of metal-doped a-C:H films that metal dopants promote the graphitization of carbon content [30]. However, other researches of Ag-incorporated a-C:H films using other deposition processes also indicated a similar irregularity at low silver content [32,33]. This irregularity could be