

# Development of silver-containing diamond-like carbon for biomedical applications. Part I: Microstructure characteristics, mechanical properties and antibacterial mechanisms

Wen-Chien Lan<sup>a,b</sup>, Shih-Fu Ou<sup>c,d,e</sup>, Ming-Hong Lin<sup>f</sup>, Keng-Liang Ou<sup>a,c,d,\*\*</sup>,  
Meng-Yuan Tsai<sup>f,\*</sup>

<sup>a</sup>Research Center for Biomedical Implants and Microsurgery Devices, Taipei Medical University, Taipei 110, Taiwan

<sup>b</sup>School of Dentistry, College of Oral Medicine, Taipei Medical University, Taipei 110, Taiwan

<sup>c</sup>Research Center for Biomedical Devices and Prototyping Production, Taipei Medical University, Taipei 110, Taiwan

<sup>d</sup>Graduate Institute of Biomedical Materials and Tissue Engineering, College of Oral Medicine, Taipei Medical University, Taipei 110, Taiwan

<sup>e</sup>Institute of Mold & Die Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung, 807, Taiwan

<sup>f</sup>Department of Mechanical Engineering and Graduate Institute of Mechanical and Precision Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung 807, Taiwan

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## Abstract

Nanosilver containing diamond-like carbon films with different silver fractions were synthesized by the radio frequency magnetron sputtering using a single silver target in an atmosphere of Ar/CH<sub>4</sub> mixture. The nanocrystalline silver clusters spontaneously segregated within an amorphous diamond-like carbon matrix. The amorphous-to-crystalline phase transformation resulted in both the surface hardness and electrical resistivity of the composite films decreasing with increasing the silver cluster size. The enlarged cluster size also increased the film surface roughness and water contact angle. All the films exhibited an anti-bacterium rate of over 93%, which evidenced that applying these composite films to anti-bacterium surface treatment is effective.

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## 1. Introduction

Amorphous hydrogenated carbon (a-C:H) films with various electrical, optical, chemical and mechanical properties can be synthesized by adjusting their compositions, hybridizations and microstructures [1,2]. They have been widely applied to protective, heat-conducting, hydrophobic, biocompatible and other functional surface treatments for decades [3–6]. Previous studies have indicated that the residual stress which the a-C:H films suffered raised with film thickness increased and it may result in film

detachment [7–10]. To overcome this problem, doping metal elements or carbides in a-C:H films have been demonstrated as an effective method to reduce the residual stress [11–15]. Furthermore, adding metal elements in a-C:H films also improves the electric conductivity of films and enables new antimicrobial functions [15–17]. Some heavy metal elements, especially silver, has a long term and environment antimicrobial ability has a limited toxicity to mammalian cells have been reported [18]. The nanoscale silver and its compounds have been proven to be effective matters against multiple drug-resistant bacteria by hindering the respiration and division of bacteria. It is generally reported that metal ions may bind to thiol groups in enzymes and proteins, and be deposited on cell membranes or cell walls which inhibit cell division and disrupt membrane integration [19–21]. Therefore, silver containing carbon

\*Corresponding author: Tel.: +886 7 3814526-5430;

fax: +886 7 3835015.

\*\*Co-Corresponding author.

E-mail address: [mengyuan6826@gmail.com](mailto:mengyuan6826@gmail.com) (M.-Y. Tsai),  
[klou@tmu.edu.tw](mailto:klou@tmu.edu.tw) (Keng-Liang Ou).

coatings have been attempted via currently carbon deposition techniques [16,17,22,23]. For extending the selectivity of substrate materials and corresponding applications, these techniques nowadays utilize a plasma enhancement to lower down the process temperature [24–31]. Among these carbon deposition techniques, radio frequency (RF) magnetron sputtering is often employed because of its low cost, simplicity and wide use. The typical magnetron sputtering deposition of carbon usually utilizes a graphite target as RF plasma cathode and introduces additional hydrocarbon gas as a supplementary carbon source. In this study, the graphite target was substituted by a silver target, and the introduced methane gas became the main carbon source for deposits. The silver content in films was controlled by adjusting the RF power input on silver target. According to previous researches [16,17,22,23], due to the fact that silver is relatively inert with carbon, the silver content in films usually segregates from a-C:H matrix and results composite behaviors. The aim of this study is to investigate the correlations between silver content and physico-chemical properties of synthesized Ag/a-C:H films and to evaluate the applicability of these composite for antibacterial usages.

## 2. Materials and methods

### 2.1. Deposition of Ag/a-C:H composite films

The substrate material is glass with a size of 1 cm in diameter and 2 mm in thickness. After being cleaned in ultrasonic bath of acetone and ethanol then air dried, glass substrates were loaded into the deposition chamber. The distance between silver target and substrates was fixed at 60 mm. The silver target had a purity of 4 N and a diameter of 7.62 cm. The sputtering system and detail deposition procedures have been described in previous works [32,33]. After evacuating the chamber and heating the substrates to 200 °C, the methane–argon gas mixture in a same ratio of 1/1.5 was introduced and the RF plasma was triggered under a working pressure of 0.23 Pa. Five different target power input, 100 W, 150 W, 200 W, 250 W and 300 W, were applied respectively to synthesize films with different silver contents. A same film thickness of 1100 nm was controlled for films prepared in all conditions.

### 2.2. Characterizations of Ag/a-C:H composite films

The surface and cross-sectional morphologies of deposited films were observed by using a scanning electron microscope (SEM, JSM-6500) and an atomic force microscope (AFM, NanoMan NS4+D3100). The compositions of deposited films were analyzed by using the Energy dispersive X-ray spectrometer (EDX) attached on the scanning electron microscope. Due to the fact that hydrogen element is out of the detection limit of EDX, the actual silver fraction cannot be quantified. The ratio of measured Ag to C was used as an index for the silver content in films.

A Raman spectrometer (BWTEK-MiniRam<sup>TM</sup>II) was used to analyze the bonding of a-C:H matrix in films. The hardness of the deposited film was measured by nanoindentation (Asmec-UNAT-M) with a diamond indenter and a load of 3 mN. The electrical resistivity of films was calculated via multiplying sheet resistivity values from 4-point probe measurement by measured film thickness. The contact angles of deionized water drop on surfaces of film with different silver content were measured by image analyzing.

### 2.3. Antibacterial test

JIS Z2801:2000 was employed as a standard to test the antimicrobial efficacy of films. The bacterial strains used in this test were Gram-positive *Escherichia coli* (ATCC 8739). A single colony of the strain was first streaked from a frozen stock using the streak plate method on nutrition agar plates. Before bacterial inoculation, the suspension was diluted using a nutrition broth to a density of  $4 \times 10^5$  CFU/ml and then dropped onto specimens for incubation at 37 °C and 95% humidity for a period of 24 h. Serial dilution of each corresponding specimen by the dilute buffer was performed to a concentration of  $10^1$ ,  $10^2$ ,  $10^3$ , and  $10^4$  fold, respectively. 1 ml of each diluted inoculums was placed onto nutrition agar plate for further culture at 37 °C for 24 h. Number of grown bacterial colonies ( $C$ ) were counted to obtain the number of bacteria adhering to the plate ( $N$ ). The antibacterial activity calculated by Eq. (1) was recognized as the antibacterial effect.

$$\text{Antibacterial rate (AR)} = 100 \times \frac{(N_2 - N_1)}{N_2(\%)} \quad (1)$$

$N_1$ : number of bacteria adhering to the tested sample after 24 h incubation.

$N_2$ : number of bacteria adhering to the blank glass substrate after 24 h incubation.

## 3. Results and discussion

The Ag/C ratio in films obtained at different target power conditions are shown in Fig. 1. The Ag/C ratio values of films deposited at target power of 100 W, 150 W, 200 W, 250 W and 300 W are 0.07, 0.20, 0.25, 1.05 and 2.50, respectively. The Ag/C ratio increases exponentially with target power. The samples of different Ag/C ratio are denoted by Ag<sub>0.07</sub>/C, Ag<sub>0.20</sub>/C, Ag<sub>0.25</sub>/C, Ag<sub>1.05</sub>/C and Ag<sub>2.50</sub>/C in following figures and descriptions. The Ag<sub>0.07</sub>/C film exhibits an amorphous feature, but crystalline silver clusters appears in films with higher Ag/C ratio. Due to the low solubility and low activity of silver to carbon, the excess silver content segregates as secondary phase in carbon matrix. This kind of nanoclusters is commonly found in similar films which are doped by low solubility metal elements [15,22–24,34] The a-C:H matrices

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