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Ceramics International 39 (2013) 8335–8340
CERAMICS INTERNATIONAL
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Surface properties of copper-incorporated diamond-like carbon films deposited by hybrid magnetron sputtering

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Received 6 February 2013; received in revised form 14 March 2013; accepted 22 March 2013
Available online 10 April 2013

Abstract

In an effort to improve the surface properties of surgical instruments in terms of corrosion resistance, mechanical strength, anti-sticking property, and anti-bacterial performance, bioactive films of hydrogenated diamond-like carbon containing different fractions of Cu were synthesized using the radio frequency plasma enhanced chemical vapor deposition with a magnetron Cu electrode in different atmospheres comprising different proportions of Ar/CH_4 mixture. The influence of the methane fraction and plasma power on the Cu content, microstructure and surface properties of the deposited films was investigated. The results show that the films included stacked nano-clusters and domains of Cu and that the size of the nano-clusters slightly increased with the Cu content and deposition time. The Cu content in the films increased with the plasma power and argon flow ratio. In addition, increasing the Cu content not only improved hardness but also roughened the surface, and consequently, increased the water contact angle of the film surface. All films exhibited a hydrophobic surface that is expected to be useful for synthesizing minimally invasive instruments.

Keywords: Films; Nanocomposites; Carbon; Biomedical applications

1. Introduction

Surgical instruments come into contact with many different types of tissues and body fluids. Therefore, materials for these instruments must have the right combination of surface properties, including corrosion resistance, proper mechanical strength, anti-sticking properties and antibacterial performances. Applying surface modifications to alter the properties of these materials is the most frequently used method for fulfilling these functional demands and the most frequently applied surface modification to promote antisticking is to coat the device with a low-surface-energy polytetrafluoroethylene (PTFE) layer. However, PTFE lacks mechanical strength and high-temperature stability and thus it cannot be used on electrosurgical electrodes, which suffer from high thermal energy and tissue sticking. Amorphous hydrogenated diamond-like carbon (DLC; a-C:H) film is smooth and has

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http://dx.doi.org/10.1016/j.ceramint.2013.03.104

high hardness, corrosion resistance, and high thermal conductivity. It is also noncytotoxic and chemically stable in biological environments [1–6]. Singh et al. reported the anti-adhesive properties of an-C:H film against glial cells and fibroblasts [7]. Zhang et al. also showed a significant decrease in the number of platelets adhered on an a-C:H film compared to ChronoFlex® or glass [8].

Commonly used techniques for the deposition of amorphous hydrogenated carbon films are plasma-enhanced chemical vapor deposition (PECVD) [9,10], ion beam deposition [11], magnetron sputtering [12,13], vacuum arc deposition [14–17], and so on. The generated plasma effectively decomposes and ionizes the hydrocarbon gas to synthesize a carbon film on the substrate surface. Properties of an a-C:H film can be easily altered by incorporating certain amounts of additional elements, such as F, N, O, Cu, Ti, Ag, and Cu [18–24]. These additional elements also enable new antibacterial functions for a-C:H films [21]. The conventional PECVD methods for obtaining metal-incorporated a-C:H films simultaneously use metal-containing and hydrocarbon precursors simultaneously, and the metal content can be altered by adjusting the flow ratio of the precursors. In our previous work, rather than using a high-cost Cu-containing precursor, we successfully combined the radio frequency (RF) plasma deposition of a-C:H and magnetron sputtering deposition of Cu under a mixed atmosphere of Ar/CH_4 to deposit antibacterial Cu-incorporated a-C:H (Cu/a-C:H) films [21]. Two parameters affect the Cu content in Cu/a-C:H films deposited via such a hybrid deposition technique: (i) argon-methane ratio and (ii) plasma power. The aim of this work is to investigate the influences of these two parameters on the obtained film properties and to evaluate their potential applicability on surgical instruments.

2. Materials and methods

A hybrid deposition process that combines RF magnetron sputtering and plasma-enhanced chemical vapor deposition was utilized to deposit the Cu/a-C:H films on SUS 304 stainless steel substrates. The details of the equipment setup have been described in previous works [21]. The SUS 304 substrates were cleaned by a sequence of cleaning procedures in an ultrasonic bath: acetone for 15 min, deionized water for 10 min, and then ethanol for 15 min. After being air-dried, the substrates were loaded into the deposition chamber. The distance between the Cu electrode and the substrates was fixed at 60 mm. After evacuating the chamber, the methane–argon gas mixture was introduced and the chamber pressure was maintained at 226.7 Pa. Two types of atmospheres comprising different Ar/CH_2 mixtures, 45.4% methane and 14.7% methane, were applied. Under each atmosphere, RF plasma was triggered by applying five different power settings, 125, 150, 175, 200, and 225 W, to deposit different films.

The surface and cross-sectional morphologies of the deposited films were observed by using a scanning electron microscope (SEM, JSM-6500F). Their compositions of deposited films were analyzed by an energy dispersive X-ray spectrometer (EDX) attached on the SEM. The microstructure of the deposited film was identified by transmission electron microscopy (TEM; Model JEM2100, JEOL Co., Tokyo, Japan). An atomic force microscope (AFM, Mobile S) was used to scan the surface morphologies and determine the surface roughness of the films.

The hardness of the deposited films was measured by Vickers microindentation (FM-100e) with a diamond indenter and a load of 10 g for 60 s. To be used for medical applications, the wettability of the material surface significantly influences the antimicrobial, biocompatible, anticoagulant, and cleaning abilities of the devices. Therefore, the water contact angle on the Cu/a-C:H film-coated specimens was also measured. The contact angles of deionized water drops on the specimen surfaces were measured by sessile drop method using a contact angle goniometer (GBX DGD-DI). To obtain good statistical average value, at least five drops were measured for each sample.

3. Results and discussion

The calculated average deposition rates of the Cu/a-C:H films obtained at different plasma powers in the two different atmospheres are shown in Fig. 1. The deposition rate was calculated by measuring the thickness of the deposited film. In the 45.4% CH_4 atmosphere, the deposition rate increased with increasing the plasma power, which is typical of sputtering processes. However, the deposition rate did not seem to change with the different plasma power in the 14.7% CH_4 atmosphere. In typical sputtering deposition, the plasma density and accompanying ion bombardment on the sputtering cathode usually increases with increasing applied plasma power, which intensifies the flux of ejected Cu species, and consequently higher deposition rate. The film compositions detected by the EDX shown in Fig. 2 indicate that Cu is the main component in the films. This indicates most of the deposition flux is contributed by the Cu cathode. However, the Cu/a-C:H ratio in both the films obtained in the two atmospheres decreased with increasing plasma power. Because Cu is chemically inert to carbon, the target poisoning effect, which is commonly seen in

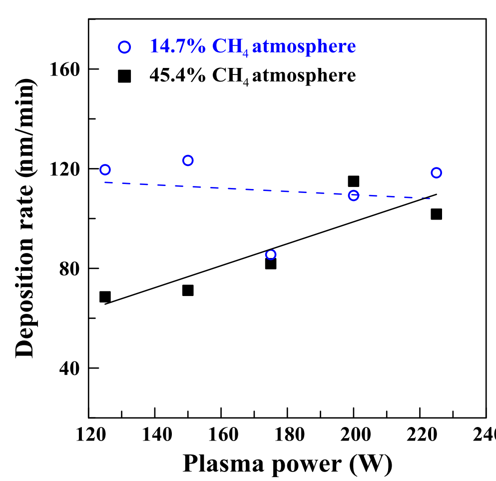

Fig. 1. Dependence of the film deposition rate as a function of plasma power for depositing Cu/a-C:H film with applying different CH_4/Ar flow ratio.

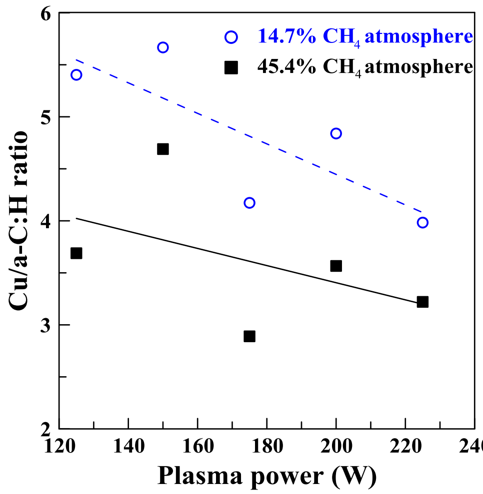

Fig. 2. Dependence of Cu/a-C:H ratio in film as a function of plasma power.

reactive sputtering, might not be the primary reason for the decrease in both the deposition rate and the Cu/a-C:H ratio in the films. This indicates that the dependence of the deposition rate on the plasma power in a hybrid deposition does not follow the trend found those in typical reactive and nonreactive sputtering processes. The reason for such irregularity of the deposition rate could be attributed to the high working pressure. The deposition working pressure in this study is near the region of PECVD processes rather than sputtering processes. The mean free path of the plasma species at such high pressure is much shorter than that in sputtering processes. Most of the Cu species ejected from the Cu cathode would be scattered during the flight from cathode to substrate. Moreover, the decomposition of hydrocarbon molecules also increases with increasing the plasma power, which accelerates the deposition rate and the fraction of the a-C:H phase. This inference explains the decrease in the Cu content ratio with increasing the plasma power. The complex interactions between the hydrocarbon molecules and electrons during plasma generation in these atmosphere mixtures could also be the reason for the irregularity of the deposition rate.

The surface images of the Cu/a-C:H films deposited at a plasma power of 175 W in a 45.4% CH_4 atmosphere for different deposition times, 10 min, 20 min, and 30 min, are shown in Fig. 3. The film seems to be stacked in nanosized clusters whose average size increases from 12 nm, 15 nm, to 30 nm with increasing deposition time from 10 min, 20 min to 30 min, respectively. This type of stacked-nanocluster morphology is commonly seen in similar films doped with metal elements with low solubility in a-C:H phase [21]. Because of the low solubility and low activity of Cu to carbon, the Cu clusters segregates as another phase that is clearly separated from the a-C:H phase. In the transmission electron microscopy (TEM) observation (Fig. 4, for example), it is found that the spherical Cu clusters are distributed a uniformly without preferred orientation. The dot-ring-like selected area diffraction pattern of the clusters demonstrates that the clusters are aggregations of face-centered cubic crystalline Cu grains. This morphology of the metallic spherical clusters not only

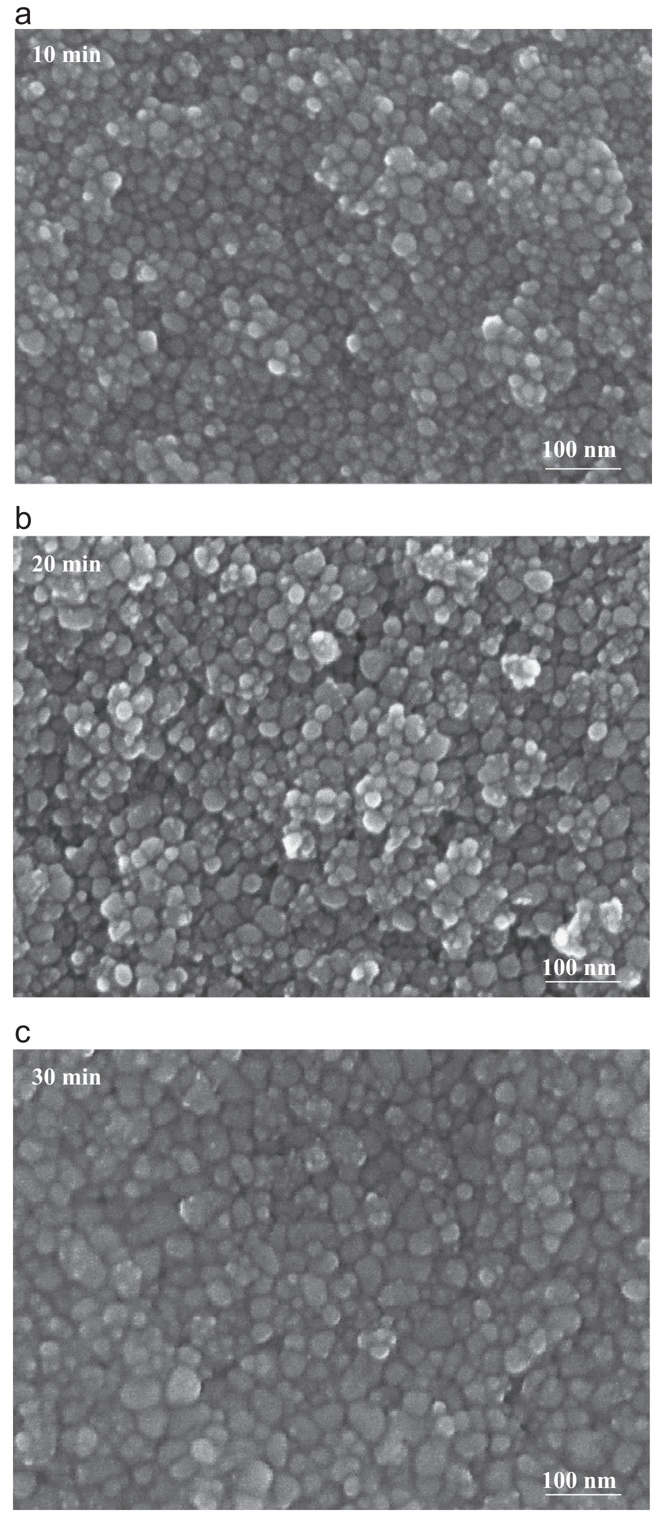

Fig. 3. SEM surface images of films deposited at plasma power of 175 W and methane flow ratio of 45.4% for (a) 10 min, (b) 20 min and (c) 30 min.

influences the surface roughness and consequent chemical properties, but also the electrical conductivity of the films.

Differences in the cluster size in the films also causes differences in the surface roughness and the roughness change has a considerable influence on the optical, tribological, and wettability performances and the consequent bacterial adhesion

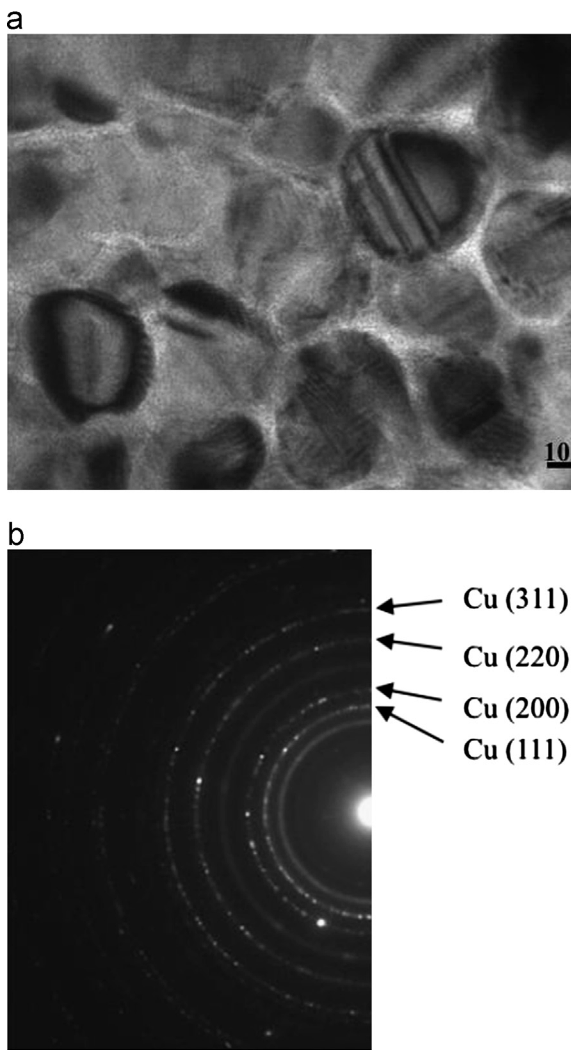

Fig. 4. (a) TEM bright-field image and (b) selected area diffraction of the film obtained at plasma power of 225 W and methane flow ratio of 45.4%.

behavior of these Cu/a-C:H composite films. Fig. 5 shows that the surface roughness of the films obtained in the two different atmospheres increases with increasing the plasma power. It is obvious that the films obtained in the 14.7% CH_4 atmosphere are rougher than those obtained in the 45.4% CH_4 atmosphere. Referring to Fig. 2, it can be found that the films obtained in the 14.7% CH_4 atmosphere contain more Cu than those obtained in the 45.4% CH_4 atmosphere. The higher fraction of Cu content may form more clusters with larger sizes, which increases the higher surface roughness.

The water contact angles on the films also reflect this surface roughness difference. In Fig. 6, the measured water contact angle on the films increases with the increasing film surface roughness, which is in keeping with the typical trend that the water contact angle usually slightly increases with increasing the surface roughness on a nano-scale. The films obtained in the 14.7% CH_4 atmosphere exhibit relatively higher water contact angles than those obtained in the 45.4% CH_4 atmosphere. This indicates that the higher Cu content in the films obtained in the 14.7% CH_4 atmosphere could be one of the reasons for stronger hydrophobic properties of the films. Both

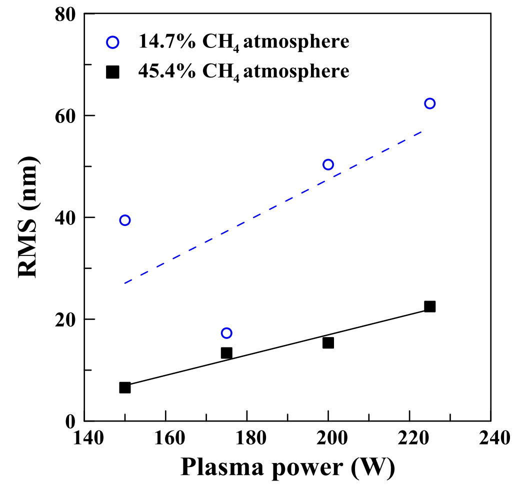

Fig. 5. Dependence of Cu film surface roughness as a function of deposition plasma power.

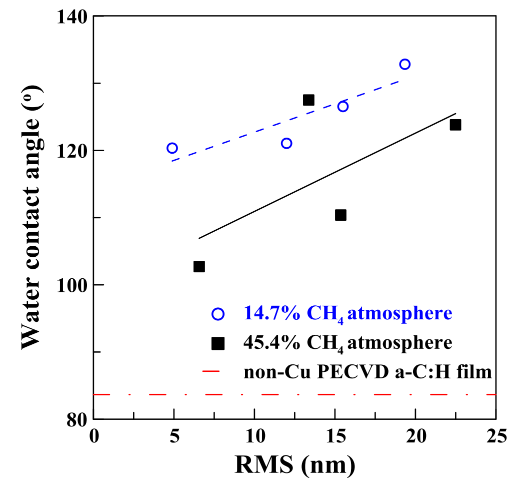

Fig. 6. Dependence of water contact angle on film surface as a function of deposition plasma power. The red line is the water contact angle on conventional PECVD a-C:H film.

the Cu content and the surface roughness enable the Cu-incorporated a-C:H films to be more hydrophobic than conventional a-C:H films. A hydrophobic surface can not only as an anti-sticking material but also for the antimicrobial applications. It is known that a hydrophobic surface can inhibit the formation of biofilms and the adhesion of bacteria. In addition, The DLC film with hydrophobicity has good hemocompatibility because it promotes less platelet spreading [25].

The surface hardness values of the films are shown in Fig. 7. All deposited specimens exhibited a higher surface hardness than that of the stainless steel substrate, but it was much lower than that of conventional PECVD a-C:H films. Surprisingly, films containing such a high fraction of relatively softer Cu do not reduce the hardness of the substrate. The films with higher Cu content in particular show even higher surface hardness values. This contrary phenomenon could be owing to the Hall–Petch hardening effect induced by compositing nanoscale clusters and a-C:H phase frames.

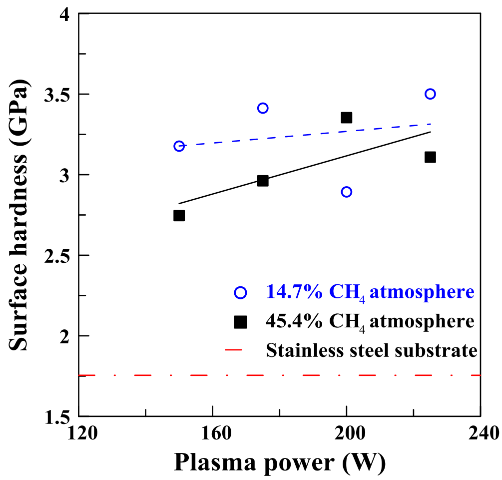

Fig. 7. Dependence of the film surface hardness as a function of deposition plasma power. The red line is the surface hardness of uncoated stainless steel substrate.

According to the above results, the segregation of Cu content and the presence of spherical nanoclusters increase not only the surface roughness and the consequent water contact angle on films, but they also raise the surface hardness of the coated specimens.

4. Conclusion

Bioactive films of hydrogenated diamond-like carbon containing different fraction of Cu were synthesized using RF plasma-enhanced chemical vapor deposition with a magnetron Cu sputtering electrode in different atmospheres comprising proportions of Ar/CH_4 mixtures. In both the 14.7% CH_4 and 45.4% CH_4 atmospheres, the Cu content in the films slightly decreased with increasing the plasma power. Cu in the films segregated as stacked nanoclusters and domains. For films obtained in the atmosphere in the 45.4% CH_4 atmosphere, the size of the nanoclusters increased slightly with increasing the deposition time and Cu content. The increased nanocluster size roughened the films surface and caused a relatively higher water contact angle. The films obtained in the 14.7% CH_4 atmosphere also showed similar trends but a relatively higher Cu content. Because the Cu contents of all the films were close to each other, the surface hardness of all the films was also close to each other; however, the surface hardness slightly increased on increasing the Cu content. All the Cu-incorporated diamond-like carbon films fabricated in this study exhibited a hydrophobic surface, which implies that they can be used as coatings on minimally invasive instruments.

Acknowledgments

The authors would like to thank the Center of Excellence for Clinical Trial and Research in Neurology and Neurosurgery, Taipei Medical University-Wan Fang Hospital for financially supporting this research under contract no. DOH101-TD-B-111-003, and supported partly by the Department of Health, Executive Yuan, Taiwan under contract no. DOH101-TD-N-111-003. The authors would also like to thank the Taipei Medical University—Shuang Ho Hospital, under grant number 99TMU-SHH-06.

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