



Structural properties and surface wettability of Cu-containing diamond-like carbon films prepared by a hybrid linear ion beam deposition technique



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ABSTRACT

Cu-containing diamond-like carbon (Cu-DLC) films were deposited on Si/glass substrate by a hybrid ion beam deposition system. The Cu concentration (0.1–39.7 at.%) in the film was controlled by varying the sputtering current. The microstructure and composition of Cu-DLC films were investigated systematically. The surface topography, roughness and surface wettability of the films were also studied. Results indicated that with increasing the Cu concentration, the water contact angle of the films changed from 66.8° for pure carbon film to more than 104.4° for Cu-DLC films with Cu concentration larger than 24.4 at.%. In the hydrophilic region, the polar surface energy decreased from 30.54 mJ/m² for pure carbon film to 2.48 mJ/m² for the film with Cu 7.0 at.%. © 2015 Elsevier B.V. All rights reserved.

1. Introduction

Due to its many superior properties, such as high hardness and low coefficient of friction, diamond-like carbon (DLC) has widespread applications [1]. However, for some unique applications, such as medical implants [2], water-repelling and surface-cleaning surfaces in special devices [3], a hydrophobic or hydrophilic surface behavior combined with other superior mechanical properties was needed, so the surface properties of DLC films have aroused much attention. Many efforts have been made to modify the surface properties of DLC films, such as incorporating a third element [4], employing surface treatment by different gas plasma [5], manipulating dual-roughness structures [6], or just changing the deposition pressures [7]. Among of those methods, the incorporation of metal elements, such as Cr, W and so on, can not only tailor the surface properties of DLC easily but also decrease the disadvantage of high residual stress [8,9].

Recently, Cu-containing DLC (Cu-DLC) films have been widely studied on its tribological, electrical and optical properties [10,11]. In particular, the surface properties of Cu-DLC films deserved very special attention. For example, Chan et al. [12] reported that Cu-DLC films offered superior antibacterial activity against *Escherichia coli*. Ivanov-Omskii et al. [13] revealed that Cu-DLC films could inhibit fungi growth at the surface. However, the relationship between structure

and surface properties of Cu-DLC with various Cu concentrations is still unclear.

In the present work, Cu-DLC films (0.1–39.7 at.%) were prepared using a hybrid linear ion beam system. The composition and microstructure of the Cu-DLC films were investigated, as well as the dependence of surface topography, roughness and surface wettability on Cu concentrations. The surface wettability was discussed in terms of the chemical composition, microstructure and surface roughness of the films. For comparison, the structure and the surface wettability of pure DLC films were also involved.

2. Experimental details

Cu-DLC films were deposited by a hybrid ion beam deposition system [9] consisting of a rectangular DC magnetron sputtering with a Cu target (99.99%) and a linear anode-layer ion sources (LIS). Prior to deposition, the base pressure was about 2.7×10^{-3} Pa. During deposition, C₂H₂ of 15 sccm was introduced into the LIS for DLC deposition. Typical values of LIS voltage and current were 1200 V and 0.2 A, respectively. The Ar sputtering gas of 65 sccm was supplied for Cu sputtering. DC sputtering current was set at 0.8, 1, 1.2, 1.5, 1.8 and 2 A to control the concentration of incorporated Cu, respectively. The work pressure was about 0.53 Pa. A negative pulsed bias voltage of -100 V (350 kHz, 1.1 μs) was applied to the substrate. The deposition time was 15 min. For comparison, the pure DLC film was prepared using LIS without operation of magnetron sputtering.

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A surface profilometer (Alpha-Step IQ, US) was applied to measure the thickness of the as-deposited films with employing a step formed by a shadow mask. X-ray photoelectron spectroscopy (XPS, Axis ultradld, Japan) was used to characterize the chemical composition and chemical bonds of the films with Al (mono) K α irradiation at a pass energy of 160 eV. Before measurement, the energetic Ar⁺ ion beam of 3 keV was used to etch the sample surface for 5 min to remove any contaminants. The Bruker D8 Advance diffractometer with monochromatic Cu K α radiation (Running condition: 40 kV, 40 mA; the wavelength: 0.15418 nm) was used to analyze X-ray diffraction (XRD) patterns in the conventional θ - θ configurations, the data were collected in continuous scanning mode with a step angle of 0.02° and a sampling time of 0.1 s.

A scanning probe microscope (Dimension 3100 V, Veeco, US) was used to study the surface topography at a scan rate of 2.0 Hz. The root-mean-square roughness (Rq) of the films was calculated from 512 × 512 surface height data points obtained from the 3 μm × 3 μm scan area with NanoScope v7.20 software, and the atomic force microscopy (AFM) analyses were performed on a tapping mode. A Scanning Electron Microscopy (SEM) (S-4800, Hitachi, Japan) was applied to investigate the plan-view morphology of the films at operating voltage 4 kV. A contact angle measurement system (OCA20, Data physics, Germany) was adopted to measure the contact angle of water and glycerol at normal room temperature and pressure.

3. Result and discussion

As the sputtering current increased from 0.8 A to 2 A, the Cu concentration, the film thickness, the average deposition rate and the sp^2 -C/ sp^3 -C ratio based on XPS spectra [14] were shown in Table 1, respectively. The sp^2 -C/ sp^3 -C ratio depended on the analysis of C 1 s peaks with the software CasaXPS; after the extraction of background with the Shirley method, the fitting of the C 1 s peaks was performed by using three main components with each component being the linear combination of a Gaussian function and a Lorentzian function.

Fig. 1(a) is the typical XPS C 1 s spectra for the films with various Cu concentrations, and Fig. 1(b) illustrates the representative Cu 2p spectra of the film with Cu 39.7 at.%. In Fig. 1(a), the C 1 s spectra can be deconvoluted into three main peaks: sp^2 -C around 284.5 eV, sp^3 -C around 285.3 eV [15] and C-O or C = O bond around 288.1 eV [16]. In the Cu 2p spectra, two peaks corresponding to Cu (2p 1/2) and Cu (2p 3/2) with binding energies at about 952.7 eV and 932.8 eV were detected [17,18], which suggested the incorporation of Cu in the DLC and no C-Cu bonding was formed.

Fig. 2 exhibits the XRD patterns of the Cu-DLC films deposited on glass with different Cu concentrations. For the film with Cu 39.7 at.%, two peaks were obtained at 2θ of 43.3° and 50.4°, which matched well with the face-centered cubic Cu phase, corresponding to Cu (111) and Cu (200), respectively [17]. However, as Cu concentration decreased, the peak of Cu (200) could not be observed, even the Cu (111) peak disappeared when the Cu concentration was less than 7.0 at.%. According to Scherrer formula [19], when the Cu concentration was

Table 1

The Cu concentration, the film thickness, average deposition rate and sp^2 -C/ sp^3 -C ratio with sputtering current.

Sputtering current (A)	Cu concentration (at.%)	Thickness (nm)	Deposition rate (nm/min)	sp^2/sp^3 ratio (%)
Pure carbon film	0	427.9	14.3	1.03
0.8	0.1	471.0	31.4	0.93
1.0	2.6	609.9	40.7	0.78
1.2	7.0	571.7	38.1	0.89
1.5	24.4	844.4	56.3	1.07
1.8	38.9	1110.6	74.0	1.08
2.0	39.7	1192.8	79.5	2.01

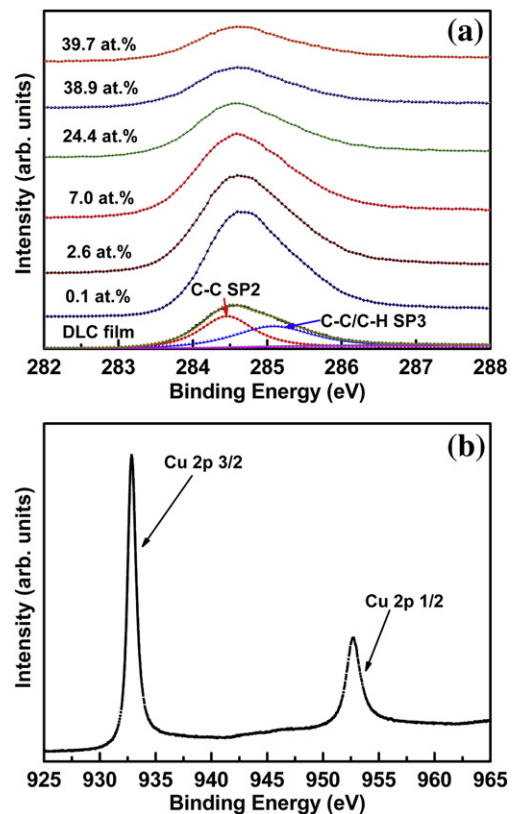


Fig. 1. Typical XPS spectra for the Cu-DLC films (a), and the representative Cu 2p spectra of the films with 39.7 at.% Cu (b).

higher than 24.4 at.%, the size of the copper crystallite based on (111) diffraction peak was about 6 nm.

Fig. 3 presents the tapping mode 2D-AFM images of the films. It can be seen that the pure DLC film illustrated a smooth surface with Rq at 0.518 nm. However, the incorporation of Cu atoms in DLC matrix led to the increase of the surface roughness, even some granular structure appeared. As the Cu concentration varied from 0.1 at.% to 38.9 at.%, the Rq increased from 1.16 nm to the maximal value of 4.13 nm. Similar surface morphology of Cu-DLC was also found in other previous studies [20–22], and the increase of surface roughness with the increasing Cu concentration can be attributed to the formation of copper crystallite [22].

To further investigate the structure evolution, the surface topography of the films was shown in Fig. 4. No distinct structure was observed (Fig. 4(a)) for the pure DLC film, but some small and spherical nanoparticles appeared in Cu-DLC films (Fig. 4(b)–(g)), and the spherical

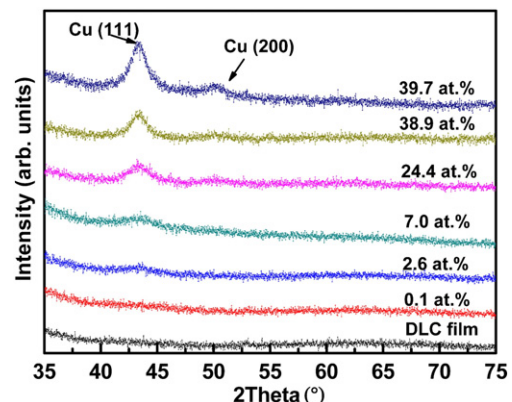


Fig. 2. XRD patterns of Cu-DLC films with various Cu concentrations.

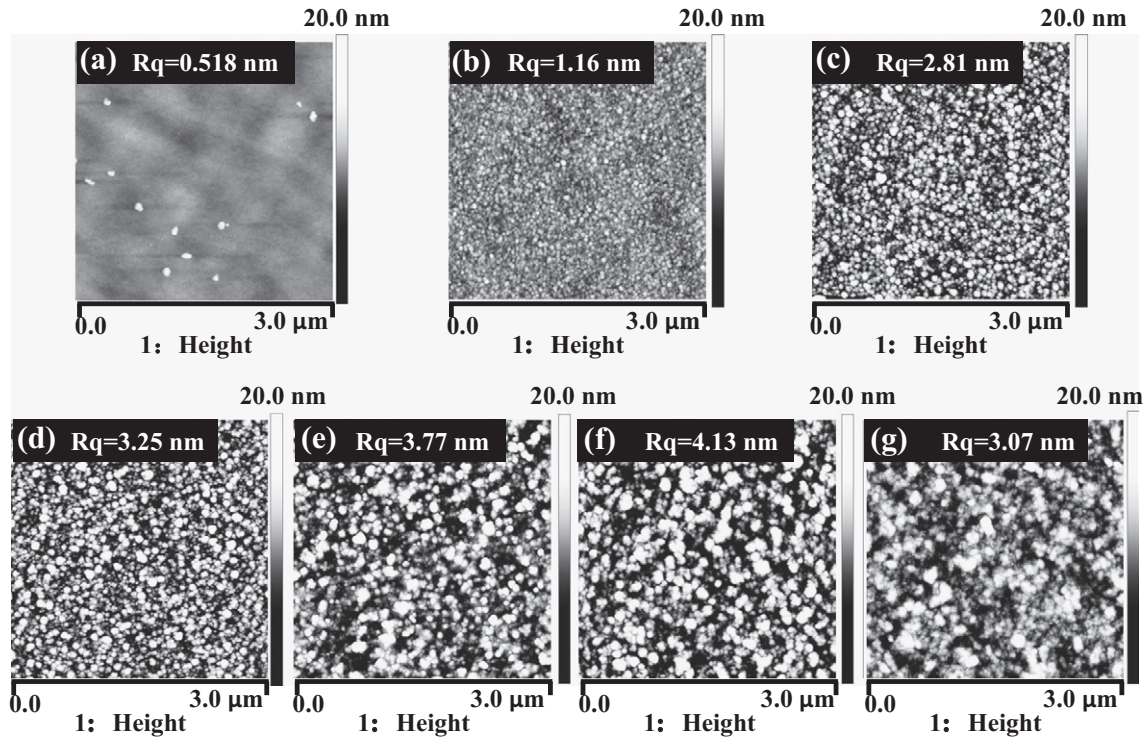


Fig. 3. Tapping mode 2D-AFM images of DLC film (a), Cu-DLC films with 0.1 at.% (b), 2.6 at.% (c), 7.0 at.% (d), 24.4 at.% (e), 38.9 at.% (f) and 39.7 at.% (g) Cu.

particulates became larger with increasing Cu concentration. Since the roughness of amorphous carbon film remained approximately constant with film thickness when deposited on Si substrate with low roughness [23], it could be said that the Cu concentration played an important role in the formation of different surface morphology for Cu-DLC films.

Since the surface morphology is closely related to the surface energy and hydrophilic/hydrophobic properties, Fig. 5(a) presents the measured contact angles of Cu-DLC films for distilled water at room temperature and pressure. Obviously, after incorporating Cu into the DLC films, the water contact angle exhibited significant changes. For pure DLC film, it was about 66.8°; while as the Cu concentration increased from 0.1 to 7.0 at.%, the water contact angle increased from 76.6° to 82.7°. When the Cu concentration was higher than 24.4 at.%, the water contact angle was larger than 104.4°, indicating the more hydrophobic surface. Moreover,

the results agreed very well with the results of measured glycerol contact angles (not shown here).

Here, surface energy is resolved into a polar and a dispersive components [7], which can be calculated by the equation proposed by Fowkes, Owens and Wendt [24]. The equation is as following

$$1 + \cos \varphi = 2\sqrt{\gamma_s^d} \left(\frac{\sqrt{\gamma_l^d}}{\gamma_l} \right) + 2\sqrt{\gamma_s^p} \left(\frac{\sqrt{\gamma_l^p}}{\gamma_l} \right) \quad (1)$$

where φ is contact angle (°); γ_s^p and γ_s^d are the polar and dispersive component of free energy of the solid (mJ/m²), respectively; γ_l is the total free energy of the liquid (mJ/m²); and γ_l^p , γ_l^d are the polar and dispersive component, respectively. The polar and dispersive of surface

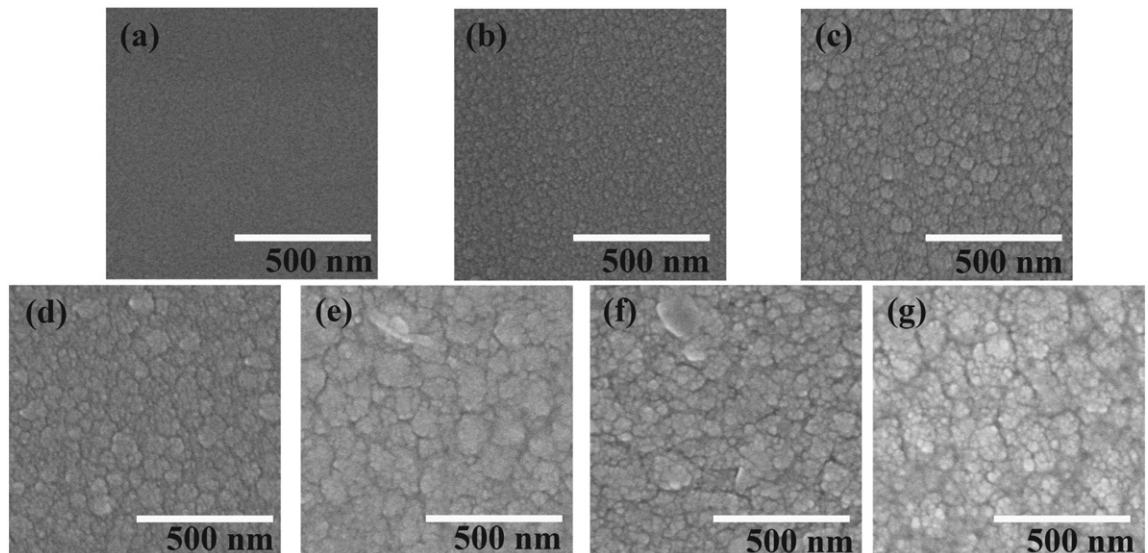


Fig. 4. Surface topography of DLC film (a), and Cu-DLC films with Cu concentration at 0.1 at.% (b), 2.6 at.% (c), 7.0 at.% (d), 24.4 at.% (e), 38.9 at.% (f) and 39.7 at.% (g).

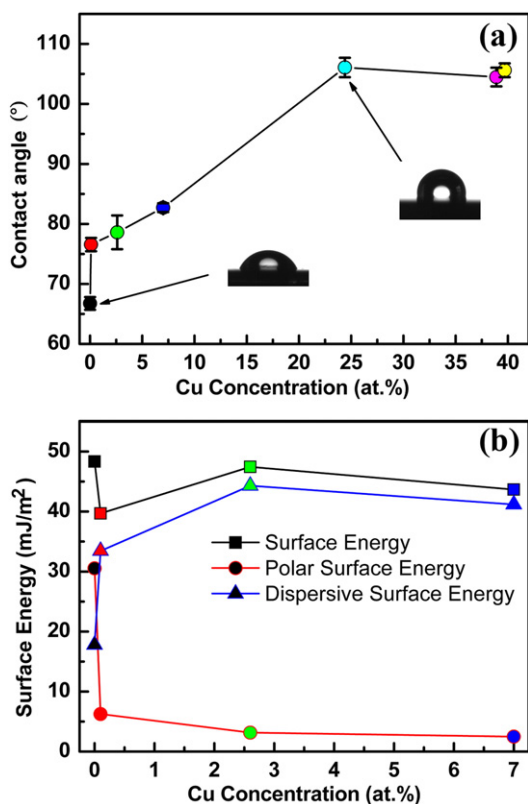


Fig. 5. Contact angles for distilled water with various Cu concentrations (a), the total surface energy with splitted polar and dispersive components in the hydrophilic region ($\varphi < 90^\circ$) as a function of Cu concentration (b).

energy of water are 51.0 mJ/m^2 and 21.8 mJ/m^2 , respectively. The polar and dispersive of surface energy of glycerol are 30.0 mJ/m^2 and 34.0 mJ/m^2 , respectively [7]. Fig. 5(b) shows the total surface energy with splitted polar and dispersive components in the hydrophilic region ($\varphi < 90^\circ$). When the Cu concentration increased from 0 to 7.0 at.%, the total surface energy did not show significant change, but the polar surface energy decreased from 30.54 mJ/m^2 to 2.48 mJ/m^2 . However, the dispersive surface energy performed an opposite trend.

According to surface energy results, it was clear that with increasing Cu concentration, the polar component in the hydrophilic region decreased significantly, as a consequence, the polar part of water molecule attracted by the film surface decreased, resulting in a larger contact angle [7]. Actually, the polar component depends on the intermolecular forces, and the reduction in the polar component may be due to the Cu oxidation on the surface and the formation of networks with less unsaturated bond, which causes the less dipolar interaction [25]. However, for films in the hydrophobic region, larger spherical particles were observed in the AFM and SEM images. Combined with the XPS and XRD results, the nanosized Cu crystallite were formed in the DLC matrix, and spherical particulates due to incorporation of the Cu atoms seemed to aggregate together to minimize the surface energy with increase of Cu concentration. The formation of spherical particulates and change of surface roughness could be explained from the deposition process of amorphous carbon. In the deposition process, metal atoms could bond together to form nucleation centers at the defects on the surface of the amorphous carbon film, and the growth in size of copper crystallite could be limited when the surface defects density was high. As the Cu concentration increased, the density of Cu crystallite and subsequently the surface roughness also increased. As a result, the spherical Cu particulates became larger [22]. The rough surface could trap air and result in a hydrophobic surface [26]. In this case, it can be concluded that the larger spherical particulates caused by higher Cu concentration may be the key

factor to the observed higher water contact angle. Similar phenomena about the relationship between water contact angle and morphology were also reported in previous studies [7].

4. Conclusions

The Cu-DLC films with Cu concentration ranging from 0.1 to 39.7 at.% were prepared by a hybrid linear ion beam deposition system with Cu target (99.99%) and C_2H_2 precursor gas. The characterization of composition and structure showed that the Cu crystallite began to evolve in the amorphous DLC matrix with higher Cu concentration. With the incorporation of Cu, the water contact angles increased from 66.8° for pure DLC film to more than 104.4° for films with Cu concentration higher than 24.4 at.%. The decrease of polar surface energy in the hydrophilic region ($\varphi < 90^\circ$) and larger spherical particles in the hydrophobic region could be the reason to the increase of water contact angle with Cu concentration.

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