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Comparative study on structure and wetting properties of diamond-like carbon films by W and Cu doping

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A B S T R A C T

By specifically selecting the carbide-forming metal (W) and non-carbide-forming metal (Cu) as the doped metal, we fabricated the W and Cu doped diamond-like carbon (W-DLC and Cu-DLC) films by hybrid ion beam system, respectively. And a comparative study on structure and wetting properties of W-DLC and Cu-DLC films was focused. For Cu-DLC films, the wettability transformation from hydrophilicity (76.56°) to hydrophobicity (105.6°) was observed. While in case of W-DLC films, the wettability of films maintained the hydrophilicity (73.6 ± 3.93°) within the presented W concentration. Based on the surface energy calculation and electronic structure analysis from first-principles calculations, we firstly gained insight into the wettability behavior of W-DLC and Cu-DLC films in terms of the bond characteristics formed between doped metal and C atoms. Results showed that the anti-bonding characteristic between Cu and C atoms reduced the polar components of surface energy and dangling bonds, contributing to the improvement of hydrophobic property, while the non-bonding characteristic for W—C bond resulted in the appearance of dipoles, leading to the hydrophilic character. It was in particularly concluded that the different bond characteristic between metal and C atoms played a key role in the wettability of metal doped DLC films. The obtained results offer a facile strategy to design DLC films with tailored wettability properties for the promising hydrophobic applications.

1. Introduction

Owing to its exceptional properties such as super-high hardness, thermal conductivity and unusual lubricity, diamond-like carbon (DLC) film has become one of the most promising engineering materials [1–2]. However, the existed high intrinsic stress and hydrophilic surface property of DLC film limit its further applications in the fields of microelectromechanical systems as stiction-reducing films [3–4]. To avoid this problem, various metal elements were usually doped into carbon matrix to adjust the properties of the film [4]. For example, introducing carbide-forming metal such as Ti into DLC films brought higher sp^2-bonded carbon and the formation of Ti—O bond, which decreased surface energy of films leading to the increase of water contact angle (WCA) from 68.5° to 105° (a material is called hydrophobic when the intrinsic WCA is >90° [5]) [6]; for non-carbide-forming metal such as Ni doped DLC film, the WCA was maintained at approximately 80° due to the partly oxidized state of Ni [7]. However, Ostrovskaya et al. [8] reported that the doped carbide-forming metals could make the films more hydrophilic, while the non-carbide-forming metals decreased the surface energy and thus led to hydrophobicity. It is obvious that, due to the complex interaction between the doped metal and carbon atoms [9], the wettability of metal doped DLC films (Me-DLC) showed distinct dependence upon the type and concentration of the doped metal, leading to the controversy of wetting mechanism. Therefore, by combining the experiment with theoretical calculation, the further comparative and systematical understanding of the correlation between the microstructure and wetting property of Me-DLC films caused by different metals is still required.

In this work, two typical metal elements, W as carbide-forming metal with non-bonding characteristic and Cu as non-carbide-forming metal with anti-bonding characteristic [9], were selected to synthesize the Me-DLC films for comparison. The effects of surface chemical properties, structure and roughness of the films on surface energy were discussed comparatively. Moreover, the first-principles simulation was also used to clarify the mechanism of wetting properties caused by W or Cu doping from atomic scale. It could provide an effective guidance for selecting doped metals to control the wettability of DLC films for

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promising applications such as biomedical implants and marine frictional components.

2. Experimental details

Cu doped DLC (Cu-DLC) and W doped DLC (W-DLC) films were deposited at room-temperature on crystalline silicon (P ⟨100⟩) using a hybrid ion beam deposition system [10] which consisted of an anode-layer linear ion source (LIS) and a DC magnetron sputtering. Prior to the deposition, the substrates were cleaned by an ultrasonic bath using acetone and ethanol for 15 min separately. When the base pressure of chamber was about 2.7×10^{-3} Pa, the substrates were cleaned by Ar ions for 10 min. During Cu-DLC films deposition, C_2H_2 of 15 sccm was introduced into the LIS for DLC deposition; the Ar gas of 65 sccm was supplied to the magnetron sputtering, and the sputtering currents were set as 0.8, 1.0, 1.2, 1.5, 1.8 and 2.0 A to control the Cu concentration. For W-DLC films deposition, C_2H_2 of 10 sccm was introduced into the LIS for DLC deposition; the Ar gas of 70 sccm was supplied to the magnetron sputtering, and the sputtering current was changed from 1.2 to 2.0 A to adjust the W concentration. The power of LIS source was 260 W, while that of sputtering source was in range of 1300–1500 W which varied with sputtering current. For comparison, pure DLC film was also deposited.

Raman spectroscopy (inVia-reflex, Renishaw) with 532 nm excitation was employed to evaluate the carbon atomic bonds of films. The surface morphology of films in a size of 3 μm × 3 μm was observed using a Scanning Probe Microscope (Dimension 3100 V, Veeco, US), on a tapping mode, and the image analysis of the roughness (Ra) was carried out from 512 × 512 surface height data points using a Nanoscope version 7.20 software. Furthermore, the chemical composition and bonds of the films were characterized by X-ray photoelectron spectroscopy (XPS, Axis UltraDLD, Japan) with Al (mono) Kα radiation, a pass energy of 160 eV was chosen for the acquisition of surveys spectra, while a pass energy of 20 eV was chosen to enhance the energy resolution for the acquisition of high resolution spectra. High-resolution transmission electron microscope (HRTEM) was performed using a Tecnai F20 electron microscope (FEI company, Netherlands), which was operated at 200 kV with a pointed-to-point resolution of 0.24 nm. The static contact angle was measured by an OCA20 optical system (Dataphysics Ltd., Germany) in atmosphere at room temperature, 2 μl droplets of de-ionized water and diiodomethane were used as the working liquids, respectively. The measurement was operated at 5 different regions on each sample. Surface energies (SE) were calculated using water as the polar liquid and diiodomethane as the nonpolar liquid.

In order to investigate the electronic structure of W—C and Cu—C systems, the spin-polarized first-principles calculations based on the density functional theory were performed, which were implemented in the DMol^3 software package. The exchange-correlation potential was defined by the Perdew-Burke-Ernzerhof parameterization and all electrons double-numerical polarization basis set was used. Atomic bonding characteristics were analyzed by the charge distribution of the highest occupied molecular orbitals (HOMO).

3. Results and discussion

3.1. Film composition

Fig. 1 shows the W and Cu concentrations of as-deposited films as a function of sputtering current, respectively. For W-DLC films, the W concentration in the films varied from 0.3 to 34.2 at.% as the sputtering current increased from 1.2 to 2.0 A, while the Cu concentration of Cu-DLC films varied from 0.1 to 39.7 at.% with the sputtering current increasing from 0.8 to 2.0 A. This indicated that the doped metal concentration could be easily tailored through adjusting the sputtering current.

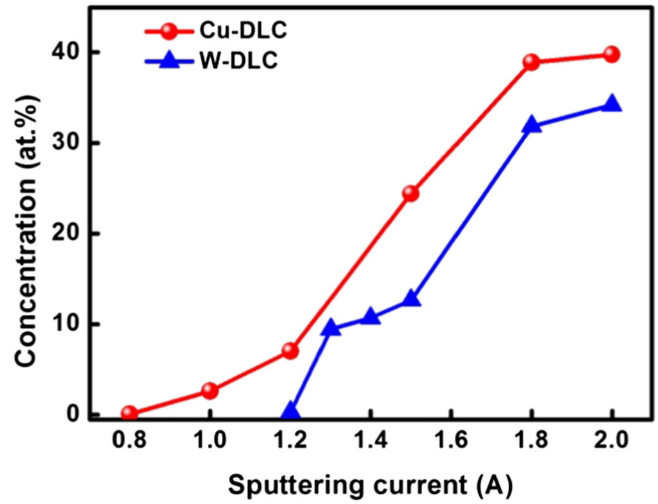

Fig. 1. W and Cu concentrations of the Me-DLC films as a function of sputtering current.

3.2. Wetting property

Fig. 2 shows the correlation between the WCA and the doped metal concentration. Pure DLC film is also evaluated for comparison. It could be seen that the contact angle of W-DLC films was approximately kept at 73.6 ± 3.93° regardless of changes in W concentrations; but for Cu-DLC films, the WCA increased dramatically (larger than 90°) when the Cu concentration was higher than 7.0 at.%. It could be deduced that, compared with pure DLC film, the DLC film was changed from hydrophilic state to hydrophobic state by the addition of Cu, while the W doping made little influence on the water wetting property of DLC films. It was revealed that the wettability of Me-DLC was strongly depended on the type and concentration of doped metals.

3.3. Microstructure

In order to explore the influence of chemical composition on wettability of W-DLC and Cu-DLC films, XPS was performed to investigate the change of surface composition [11]. Fig. 3a presents the C 1s spectra of Cu-DLC films with various Cu concentrations. The XPS C1s spectra showed a large asymmetric peak suggesting the existence of carbon atoms with various bonding states. Meanwhile, the Cu 2p spectrum of Cu-DLC film with Cu 39.7 at.% is given in Fig. 3b. There were two

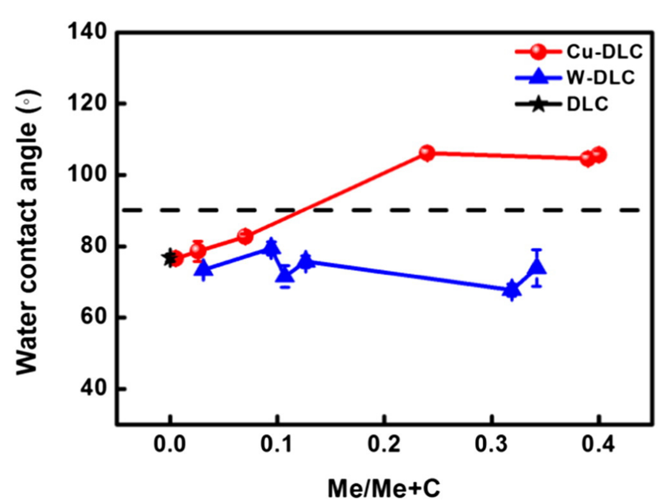

Fig. 2. Effect of W and Cu concentrations on water contact angle, and pure DLC film was also used for comparison.

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