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Microstructure and mechanical property of diamond-like carbon films with ductile copper incorporation

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ABSTRACT

In this paper, a ductile and non-carbide former Cu was incorporated into diamond-like carbon (DLC) films to modify the microstructure and property of the films using a hybrid ion beam system comprising an ion beam source and a magnetron sputtering unit. The composition, microstructure, residual stress and mechanical property of the DLC films with Cu doping were characterized carefully using X-ray photoelectron spectroscopy, transmission electron microscopy and Raman spectroscopy, stress-tester, and nanoindentation as a function of Cu concentration. The results reveal that the doped Cu atoms had low solubility in the as-deposited DLC films. The maximum solubility was found to lie around 1.93 at.%. When the Cu concentration was lower than this solubility, the doped Cu atoms dissolved in the carbon matrix, and the film exhibited the typical amorphous structure of DLC and showed a low residual stress and high elastic recovery due to the dissolved Cu atoms which could play a role of the interstitial atoms for stress relaxation through the distortion of the atomic bond length and angle. As the doped concentration exceeded the solubility, Cu nanocrystalline was formed in the carbon matrix, which could significantly improve the elastic resilience of the film through strain release via sliding of the nanocrystalline in the amorphous carbon matrix. It is worth noting that when the doped Cu concentration approached the solubility limit, amorphous nano-clusters were formed in the carbon matrix due to the segregation of Cu, resulting in the decrease of the number of the interstitial atoms, and thus caused the increase in the residual stress and the decline in the elastic recovery.

1. Introduction

Diamond-like carbon (DLC) are well known for their outstanding properties such as high hardness and wear resistance, low friction coefficient, good anti-corrosion properties and bio-compatibility with the human body, and smooth surfaces. These excellent properties and their combination are very promising for a variety of technical applications such as applications in cutting tools and dies, magnetic data storage, micro-electromechanical devices, and biological implants [1–4]. However, a limited number of industrial utilization of DLC films were taken due to their low toughness and high compressive stress which tended to cause embrittlement and exfoliation of the films from substrates. Metal element doping has been considered to solve the problems of DLC films [5–7]. Generally, the metal atoms incorporated into the DLC matrix can form nano-clusters or bond with carbon atoms in case that the concentration of the doped metal is adequately high [8,9]. These nanostructures embedded in the DLC matrix will significantly affect the microstructure and thus the properties of the DLC films.

So far numerous metallic components (Ti, Cr, Ag, Al etc.) have been used to modify DLC films [10–13]. Among these metal elements, the weak carbide former atoms, like Ag and Al, are incorporated into DLC and tend to form ductile metal phases in the carbon matrix, which have be expected to overcome the brittleness and improve the toughness of the DLC films [14,15]. Toughening significantly correlates with the composite structures of the doped metal atoms that can be nanocrystalline (or nanoparticle) or amorphous cluster in the amorphous carbon matrix. In case of nanocrystalline embedment, the toughening is obtained through strain release via sliding of the crystallites in the carbon matrix. In case of amorphous embedment, the toughening is realized through relaxation of stress via plastic deformation of the carbon phase [16]. This means that the toughening effect significantly depends on the existence form of the doped metal atoms in DLC films, which can be tailored by varying the nature and level of the doped metal atoms [14,16,17].

Copper is a ductile metal and non-carbide former, and has been considered to be a strong candidate element for reducing residual stress and improving the mechanical, tribological and biological properties of the DLC films [18–20]. In this paper, Cu was incorporated into the DLC films with different concentrations ranging from <1 up to 47 at.% using a hybrid ion beam system comprising an anode-layer linear ion

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beam source (LIS) and DC magnetron sputtering unit. The evolution of the composition and microstructure of the Cu-DLC films were studied with increasing Cu concentration. The residual stress and mechanical properties including the elastic modulus, hardness and elastic resilience of the films were systematically investigated according to the microstructures of the films. The relationships between the microstructure, residual stress and mechanical properties were discussed in detail.

2. Experimental details

A series of Cu-DLC films were deposited on 525 ± 15 μm thick silicon wafers using the hybrid ion beam system comprising LIS and DC magnetron sputtering unit equipped with a Cu target (99.99%). A schematic of the hybrid ion beam system and preparation process might be referred to in the previous work [21]. A gas mixture of C_2H_2 and Ar with a ratio of 65/15 (sccm) was introduced into the chamber as the carbon precursor and sputtering gas. Typical values of the work voltage and current of the linear ion source were 1600 ± 100 V and 0.2 A, respectively. DC power (under current control mode with a work voltage of ~400 V) with various currents in the range of 0.5–3 A was supplied to the magnetron sputtering unit to control the Cu target sputtering and thus adjust doped Cu concentration in the DLC films. The work pressure was kept at a constant of ~0.5 Pa. A pulse negative bias voltage of −50 V (350 kHz, 1.1 μs) was applied on the substrates. Two rounds of experiments have been carried out. The first round was done for measuring growth rates of the films. One the second one, the deposition times were adjusted according to the growth rates of the films to obtain a constant film thickness of 600 ± 20 nm for all samples.

A surface profilometer (Alpha-step IQ, US) was used to measure the thicknesses of the deposited films through a step between the films and Si wafers covered with a shadow mask. The composition and chemical bonds of the Cu-DLC films were analyzed using an X-ray photoelectron spectroscopy (XPS) (Axis ultraDLD) with Al (mono) Kα irradiation at a pass energy of 160 eV. Before commencing the measurement, the sample surfaces were cleaned using an Ar^+ ion beam with an energy of 2 keV for 5 min to remove any contaminants. The Cu concentration in the films was calculated according to the relative Cu, C and O atomic ratios which were determined based on the atomic sensitivity factors and the relative area ratios of the peaks in XPS spectra of the films. For simplicity, the hydrogen concentration in the films was neglected due to the lack of signal intensity in the current XPS detection measurement. Transmission electron microscope (TEM, Tecnai F20, FEI company), operated at 200 keV with a point-to-point resolution of 0.24 nm, was employed to study the microstructures of the films. The TEM specimens were directly deposited on freshly cleaved single-crystal NaCl wafers with thicknesses of about 80 nm, and subsequently were peeled off by dissolving the NaCl wafers in deionized water. The carbon atomic bond details of the films were characterized using Raman spectroscopy with incident light from an Ar^+ laser at a wavelength of 514.5 nm.

The residual stresses of the films were calculated via the Stoney equation [22], where the curvature of the film/substrate composite was determined by a laser tester. The specimens for stress test were deposited on 285 ± 5 μm thick silicon wafer strips of size 3 mm × 35 mm. The hardness and elastic modulus were measured by a nano-indentation technique (MTS-G200) in a continuous stiffness measurement mode with a maximum indentation depth of 500 nm. The characteristic hardness of the films was chosen in the depth of around 1/10th of the film thickness to minimize the substrate contribution. Six replicate indentations were operated for each sample.

3. Results and discussion

Fig. 1 shows the Cu concentration and the average growth rate of the films as a function of the sputtering current of the magnetron sputtering unit with Cu target. It can be seen that the Cu concentration of the deposited films continuously increased from 0.74 to 47.6 at.% as the sputtering current increased from 0.5 to 3 A, indicating that the doped Cu concentration in films can be controlled through adjusting sputtering current. Note that the variation in the growth rate with the sputtering current was similar to that for the Cu concentration. The growth rate of the films increased from 11.5 to 16.2 nm/min as the current increased from 0.5 to 3 A. It seems that the magnetron sputtering would improve the growth rate of the films deposited by the hybrid ion beams, consisting with our previous results of other metal atoms doping DLC films [13,23].

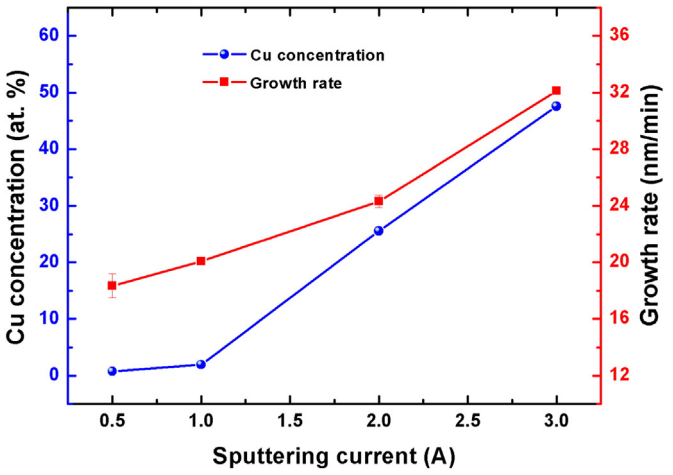

Fig. 1. Cu concentration and growth rate of the Cu-DLC films as a function of the sputtering current.

The chemical bonds of the films with different Cu concentrations were analyzed by XPS and the corresponding high-resolution C 1s and Cu 2p core level spectra are shown in Fig. 2. It can be seen from Fig. 2(a) that, the intensity of the Cu 2p peak increased with increasing Cu concentration. All the spectra presented a symmetrical sharp peak centered at ~932.2 eV, as expected for the $2p_{3/2}$ state of the metallic Cu. A small peak at 933.3 eV deconvoluted from the major peak could be assigned to Cu—O bonds. Fig. 2(b) illustrates the corresponding high resolution C 1s spectra of the films. The C 1s spectra could be deconvoluted into two strong and one weak intensity peaks around 284 eV, 285 eV and 286.8 eV, corresponding to sp^2—C, sp^3—C and C—O bonds, respectively [24,25]. Because Cu is the non-carbide former, and immiscible with carbon, Cu—C bonds were not observed in present experiments. The presence of Cu—O and C—O peaks was due to the existence of oxygen, which may be attributed to two facts: the residual oxygen in the chamber and the sample exposure to air before XPS tests. The XPS results demonstrate that the main chemical form of the incorporated Cu in the DLC films is metallic state.

The bonding fractions of the sp^2, sp^3 and C—O bonds in films were determined by the relative peak areas of the fitted peaks of Fig. 2(b) and are presented in Fig. 3. It can be seen that the sp^3 bond showed a sharp increase as Cu concentration increased from 0.74 at.% to 1.93 at.%, followed by a relatively stable value of approximately 58%, while the sp^2 bond changed in the opposite trend simultaneously. The C—O bond had remained fairly constant with a value of approximately 2.5%. It was supposed that there was a critical Cu concentration between 0.74 at.% and 1.93 at.% at which a microstructure transition in the carbon atomic bonds (sp^2 and sp^3 bonds) occurred due to the Cu incorporation.

In order to obtain insight into the microstructure evolution of Cu-DLC films as a function of the doped Cu concentration, a TEM measurement was made. Fig. 4 shows the TEM micrographs and corresponding selected area electron diffraction (SAED) patterns of the DLC films with various Cu concentrations. It can be seen that the TEM picture and the corresponding magnified view of the film with 0.74 at.% Cu (Fig. 4(a) and (b)) exhibit dense and smooth granular contrasts, and

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