Diamond & Related Materials 68 (2016) 1–9

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Synergistic effect of Cu/Cr co-doping on the wettability and mechanical properties of diamond-like carbon films

Lili Sun [a,b], Peng Guo [a], Peiling Ke [a], Xiaowei Li [a,*], Aiying Wang [a,*]

[a] Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, PR. China
[b] University of Chinese Academy of Sciences, Beijing 100049, PR. China

ARTICLE INFO

Article history:
Received 8 April 2016
Received in revised form 10 May 2016
Accepted 20 May 2016
Available online 24 May 2016

Keywords:
Co-doping
Synergistic effect
Wettability
Surface energy
Diamond-like carbon

ABSTRACT

By choosing carbide-forming element Cr and non-carbide-forming element Cu as co-doped metal elements, we firstly fabricated Cu and Cr co-doped diamond-like carbon (Cu/Cr-DLC) films using a facile hybrid ion beam deposition system. The effect of Cu/Cr co-doping on wettability and mechanical properties of DLC films were focused. The resultant Cu/Cr-DLC films were shown to afford good hydrophobicity and superior mechanical performance. In particular, the film with $Cu_{11.88\%}Cr_{6.57\%}$ (at.%) exhibited a relatively high water contact angle of 103.6°, lower residual stress of 0.89 GPa and high hardness of 13.44 GPa. The combined structural analysis demonstrated that the synergistic Cu/Cr co-doping resulted in the critical and significant relaxation of distorted C—C bond length, which ultimately caused the reduction in residual stress. Due to the formation of hard Cr carbide nano-particles in amorphous carbon matrix, the films maintained the high value of hardness. In addition, noted that the interesting wetting variety from hydrophilic to hydrophobic state was attributed to the enhanced surface graphitization and emergence of copper oxidation phases, and the film topographical microstructure could also promote the hydrophobicity of film when the maximum height of roughness was in a certain range. These results provide an expected robust synthesis method to make DLC film a promising protective coating for long lasting hydrophobic application and related harsh fields.

1. Introduction

Wettability of solid is a very important surface characteristic influencing a large range of material applications [1–2], such as anti-fogging [3], water-oil separation [4], self-cleaning [5] as well as drag reduction [6]. Amount of experimental results and theoretical calculations have confirmed that the wettability of solid surface depend on the surface free energy and the geometrical structure to a great extent [7–8]. However, if one keeps in mind the long lifetime durability and versatile low cost techniques, to develop the materials with low surface free energy together with excellent mechanical performance are still remaining the great challenge till now [9–10]. In particularly, when the mechanical components are exposed to the harsh conditions such as corrosion seawater, grave sand, and high moving speed etc. for related marine applications, the materials suffering from the serious corrosion and wear problems are required high hardness and good hydrophobicity.

Diamond-like carbon (DLC) films are one of the most promising candidates for the wide range of applications due to their extreme hardness, low friction, superior biocompatibility and chemical stability. However, the high compressive stress, poor adhesion to particular metal substrates and hydrophilic surface of DLC films are the key obstacles for their usage. Combined with hydrophobic wettability properties, DLC films have showed great possibility in applications of bio-robot, bio-medical devices and wear protection of MEMS surfaces [1,11–14]. Many efforts have been devoted so far to reduce compressive stress and improve the hydrophobicity of DLC films, wherein doping transition metal atoms into the amorphous carbon matrix is considered as an effective way to achieve the combined high performance by taking full advantage of the formed nanoparticulates of metal or metal carbides [15–16]. For instance, elements like Fe, Ni, Cu, Ti and Cr have been used to directly control the wettability as well as the mechanical properties of DLC films [17–21]. For a non-carbide-forming element, Cu doping led to the increase of water contact angle in DLC films. The hydrophobic feature attributed to the formed Cu nanoparticles, which had no advantage to generate dipole or saturate dangling bonds [19,21]. But both the stress and hardness of the film reduced drastically. On the other hand, adding carbide formed metal such as Cr or Ti into amorphous carbon matrix led to the stress reduction significantly without serious change of hardness, but decreased the water contact angle of film [20–21]. In view of the results described above, surface wetting behavior and mechanical property of DLC films shows distinct dependence upon the elemental features of doped metal. Especially, few efforts were devoted

---

* Corresponding authors.
E-mail addresses: lixw@nimte.ac.cn (X. Li), aywang@nimte.ac.cn (A. Wang).

http://dx.doi.org/10.1016/j.diamond.2016.05.006

to developing the novel materials by taking the concept of synergistic effect from co-doped metals, in which both the residual stress and surface wettability could be optimized simultaneously according to the various demands of applications.

Based on our previous simulation results [22], where most of important result was that the anti-bonding feature of Cu element and nonbonding Cr element were selected to be co-doped into amorphous carbon matrix to reduce residual stress, we firstly brought forward the concept of Cu/Cr co-doped DLC films which could improve the mechanical properties and lower residual compressive stress of DLC films obviously by Cu/Cr co-doping. So in this work, the Cu/Cr co-doped DLC films were deposited by a hybrid ion beam system. The co-doped Cu/Cr concentration in DLC films was controlled by varying the sputtering current from 1.5 to 2.5 A. The effect of co-dopants on the surface wettability and mechanical properties of DLC films was investigated. In particular, the mechanism of wetting behavior was intensively discussed in terms of the surface energy and atomic bond structure of deposited films.

2. Experimental

2.1. Sample fabrication

Cu/Cr-DLC films were deposited on Si (P ⟨100⟩, 0.0015 Ω·cm) substrates by a hybrid ion beam deposition system [20], which combined an anode-layer ion beam source (LIS) and a rectangular DC magnetron sputtering with a composite Cu/Cr target (Jiangxi Ketai advanced material CO., LTD., 3N) at 1:1 atomic ratio. The LIS source enabled the facile deposition of DLC films by decomposing the hydrocarbon gas of C_2H_2, while the sputtering source benefited the versatile deposition of Cu/Cr co-doping by introducing Ar gas. Prior to deposition, the substrates were cleaned ultrasonically in acetone and ethanol for 15 min separately. After that, the substrates were located in the substrate holder with a distance about 15 cm from the center between metal target source and ion source. A base pressure of deposition chamber was about 2.7×10^{-3} Pa. In order to remove the surface adhered impurities, the substrates were thereafter cleaned by Ar ions for 10 min (etching thickness was about 115.5 nm). During deposition, the films were prepared for 15 min in the mixture precursors with 15 sccm C_2H_2 gas and 65 sccm Ar gas. In order to introduce the metal elements in carbon matrix without destroying the nature of amorphous carbon matrix, we in particular focused the metal doping on the small amount of metal concentration in the present work. Therefore, the Cu/Cr concentration was controlled by varying the sputtering current in a range of 1.5–2.5 A. The typical current of the LIS source and working pressure were 0.2 A and 0.6 Pa, respectively, and the power of the LIS source was 260 W, while that of sputtering source was in range of 1300–1500 W which varied with different sputtering currents. Meanwhile, a pulsed negative bias voltage of −100 V with 350 kHz was applied to the substrates during both the etching and deposition process.

2.2. Characterization

Thickness of the films was measured by a surface profilometer (Alpha-Step IQ) employing a step made by a shadow mask. The surface microstructure and Cu/Cr concentration of the films were analyzed comprehensively by field emission scanning electron microscopy (SEM) equipping with an energy dispersive X-ray spectroscopy (EDS, Hitachi S-4800). 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), and the atomic force microscopy (AFM) analyses were performed on a tapping mode, where the image analysis was carried out using a Nanoscope version 7.20 software. Raman spectroscopy (inVia-reflex, Renishaw) with 532 nm excitation wave length was employed to evaluate the carbon atomic bonds of films. Furthermore, the chemical composition and bonds of the films were characterized by X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Thermo) with Al (mono) Kα irradiation. In order to get the accurate information of the surface, the measurement was taken directly without Ar^+ etching after taking from the chamber. High-resolution transmission electron microscope (HRTEM) of the DLC films was performed using a Tecnai F20 electron microscope (FEI company, Netherlands), which was operated at 200 keV with a pointed-to-point resolution of 0.24 nm. Mechanical properties were measured by the nano-indentation technique in a continuous stiffness measurement (CSM) mode with a maximum indentation depth of 300 nm. Six replicate indentations were made for each sample. The residual stress of the films was calculated from the curvature of the film/substrate was measured by a stress tester using a laser reflection method.

2.3. Wettability measurement and surface energy calculation

Static contact angle measurements were carried out by an OCA20 optical system (Dataphysics Ltd., Germany), 2 μl droplets of de-ionized water and glycerol (Gl) were used as the working liquids in atmosphere at room temperature, respectively. The test was operated at five different regions on each sample. Generally, the surface energy of liquid or solid phase can be expressed by the addition of dispersion component and polar component, and the surface energy together with its polar and dispersive components can be finally quantified by the two liquids' components according to Fowkes model [23] and Owens-Wendt-Kaelble (OWK) model [24], the details about the mechanisms of the

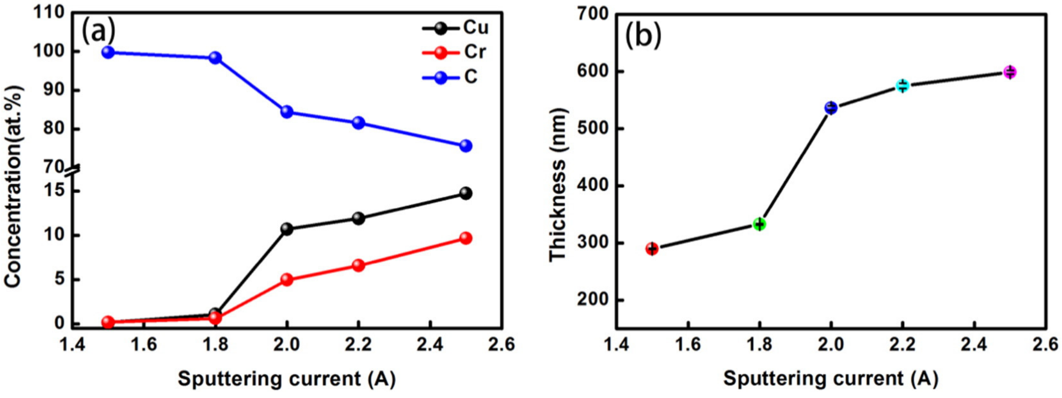

Fig. 1. (a) Composition and (b) thickness of the films as a function of sputtering current.