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Structure and properties of Mo-containing diamond-like carbon films produced by ion source assisted cathodic arc ion-plating

L.L. Wang[a], R.Y. Wang[b], S.J. Yan[a], R. Zhang[a], B. Yang[b], Z.D. Zhang[a], Z.H. Huang[a], D.J. Fu[a,*]

[a] Key Laboratory of Artificial Micro- and Nano-Materials of Ministry of Education and School of Physics and Technology, Wuhan University, Wuhan 430072 China
[b] School of Power & Mechanical Engineering, Wuhan University, Wuhan 430072, China

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ABSTRACT

Ion source assisted cathodic arc ion-plating was used to synthesize molybdenum containing diamond-like carbon films. The element of molybdenum is uniformly distributed in our sample as analyzed by Rutherford backscattering spectroscopy. The surface morphology of the films was analyzed by scanning electron microscope and atomic force microscope. The structure and bond state of the molybdenum containing diamond-like carbon films were characterized by X-ray diffraction, high resolution transmission electron microscopy, Raman spectra, and X-ray photoelectron spectroscopy. The Mo content in the films was controlled by varying of the acetylene gas flow rates. The root-mean square roughness of the as-deposited sample was found in the range of 1.5 nm. The hardness of 35 GPa has been achieved at the optimum conditions of synthesis. This can be attributed to formation multilayer structure during deposition process and the formation of hard molybdenum carbide phase with C=Mo bonding. The results show that ion source assisted cathodic arc ion-plating is an effective technique to fabricate metal-containing carbon films with controlled metal contents.

1. Introduction

A great attention was devoted to the diamond-like-carbon (DLC) films due to their outstanding properties, such as high mechanical strength and hardness, excellent chemical inertness, and exceptional friction and wear performance [1]. Its application in electronic chips, optical tools and devices, biology and medicine as protective coatings of sensors were studied by introducing new variables during the synthesis process [2]. DLC coatings also have applications in orthopedics, cardiovascular components, and waveguide because they are very hard, have low friction, are fully biocompatible and prevent leaching of metallic ions into the body [3]. In recent years there has been much interest in metal-containing carbon (Me-C:H) films. Their mechanical, tribological, magnetic, electrical, and optical properties have been widely studied. It is known that these properties are closely related to their microstructures [4]. Among them the transition metal carbides TiC, WC and NbC are interesting group of nanocrystalline materials. The conventional coarse-grained materials of the transition metal carbides show high hardness, high melting points, and chemical inertness making them useful as wear-resistant materials. In addition, several transition metal carbides such as WC and MoC also have a catalytic activity comparable to the platinum metals suggesting potential use in many catalytic processes [5]. Addition of transition metal atoms in the carbon network can enhance adhesion between the DLC films and the substrates, and can reduce the intrinsic compressive stress of the films by forming metallic crystalline domains and metal-carbon nanocomposites [2].

DLC coatings were deposited by many methods using variety carbonaceous precursor materials. For example, ion implantation [6], pulsed laser deposition [7], filtered cathodic arc deposition, magnetron sputtering [8], and RF plasma activated chemical vapor deposition [3]. A drawback to pulsed laser deposition (PLD) is that occasionally droplets or chunks of the target material are ablated and cause a surface roughness that is not easily removed [3]. The disadvantages for ion implantation are crystalline damage of the substrate, low productivity and high expenditure of the equipment. High deposition temperature and low growth rate are the main drawback to chemical vapor deposition. Sputtering and cathode arc are preferred by industrial produce. However, sputtering always shows drawbacks of low-usage of the targets, instability of the plasma and low film growth rate, so now industrial produce more and more trend to cathode arc due to high ionization ratio, high plasma intense and fast growth rate [9]. Acetylene, methane, and graphite target were usually used as the carbon source of the DLC film in cathode arc deposition process. Acetylene is the preferred gas for low pressure deposition, because its strong C≡C bond means it has a simple dissociation pattern [9].

* Corresponding author.
E-mail address: djfu@whu.edu.cn (D.J. Fu).

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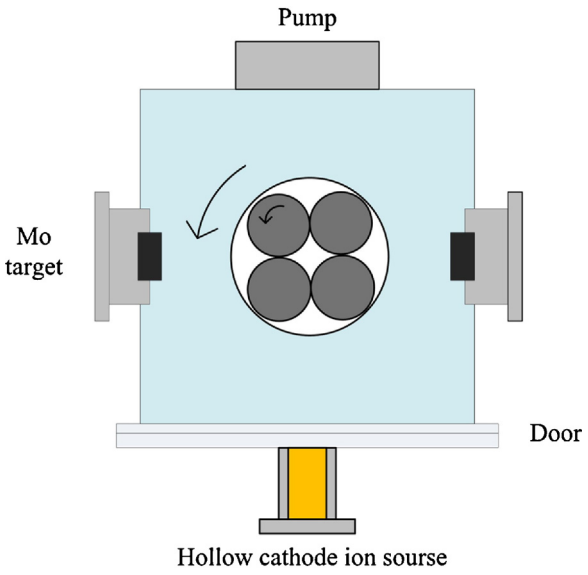

Fig. 1. Schematic diagram of the ion source assisted cathodic arc ion-plating system.

In this work DLC films containing transition metal Mo were prepared by ion source assisted cathodic arc ion-plating using acetylene gas. The aim of this article is to show the possibility of increasing [1,10] of hardness by formation of the multilayered DLC structure and investigate its microstructure and mechanical properties.

2. Experiment details

2.1. System description

The top view schematic diagram of the ion source assist cathodic arc ion-plating system is shown in Fig. 1. The acetylene gas as the carbon source was introduced into the chamber through the hollow cathode and was ionized by the plasma. The hollow cathode ion source used in this work is to ensure the full ionization of the acetylene gas and the restrictions of the plasma to offer high dense ions on the other hand. The holder is used for fixing the substrates and it can rotate to ensure the uniform growth of the films.

2.2. Film deposition

Mo containing DLC films were deposited on silicon (1 0 0) wafers, cemented carbides, and stainless steel substrates using ion source assisted cathodic arc ion-plating system with a Mo target and a hollow cathode ion source. The carbon source was offered by the hollow cathode through ionizing acetylene gas. The substrates were cleaned sequentially in methanol, ethanol, and deionized water, in each for 5 min at 60 °C, and then dried with nitrogen gas. The substrates were placed vertically on a rotating sample holder in the center of the chamber. The pressure of the chamber was better than 7×10^{-3} Pa and the temperature above 300 °C before deposition. A high bias voltage of −1000 V was applied to the substrate and the Mo target current set at 80 A to offer high energy ions, the substrate were further cleaned by this ions at the beginning of the deposition for 10 min. A bias voltage of −100 V was added to the substrates with 80% duty cycle and the chamber pressure was kept at 1.2 Pa during the film deposition process. A transition layer of Mo lasted 5 min was deposited onto the substrates to enhance the adhesion of the Mo-DLC films with substrates. The films were deposited 60 min under fixed current of 70 A of the Mo target and 50 A of the hollow cathode with different acetylene flow rate (0, 50, 100, 150, 200 sccm). Argon gas was introduced in order to maintain the pressure of 1.2 Pa during deposition process. The temperature was kept at around 300 °C during DLC films deposition process and decreased to room temperature after deposition. The distance between substrates and targets is about 10 cm.

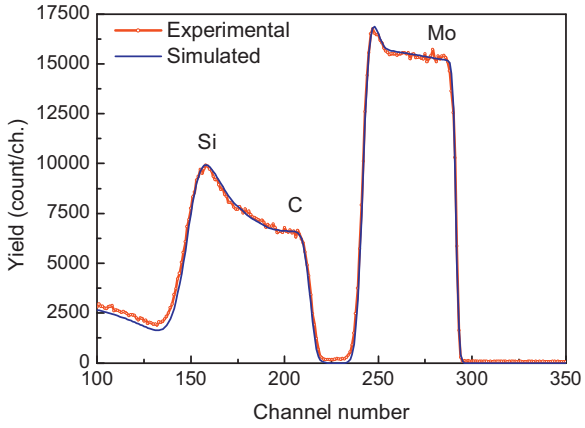

Fig. 2. Proton beam backscattering spectrum of Mo-DLC film at C_2H_2 flow rate 100 sccm on Si substrate with the thin Mo film as transition layer.

2.3. Characterization

The Rutherford backscattering spectroscopy (RBS) technique was carried out using a 1.74 MeV proton beam to determine the Mo and C contents as well as the film thickness. The scattered protons were detected at a backscattering angle of 170° by a silicon surface barrier detector with an energy resolution of ~15 keV and an effective detection area of 50 mm^2. The distance between the detector and the sample is 112.6 mm and the solid angle Ω is 3.94 msr. Spectral analysis was carried out using the iterative analytical simulation code SIMNRA. The surface morphology of the films were analyzed by field emission scanning electron microscope (FE-SEM) with EDAX genesis 7000 EDS system and SPM-9500J3 atomic force microscope (AFM) manufactured by SHIMADZU. The crystallinity and microstructure were analyzed by X-ray diffraction (XRD) performed on D8 advanced X-ray diffractometer with a Cu $K\alpha$ radiation (0.154 nm) and JEM-2010FEF (HT) transmission electron microscope operated at 200 kV. An RM-100 confocal Raman Micro-spectrometer with Ar^+ laser excitation (632.8 nm) was used to determine the content of sp^3 hybrid bond. The electron binding energy in C1s and Mo3d orbits was detected by XSAM800 X-ray photoelectron spectroscopy using Mg $K\alpha$ excitation (1253.6 eV). The microhardness were measured by using a HX-1000 Vickers microhardness tester on a load of 25 g. Ten random indentation measurements were conducted and the mean value was calculated for each sample.

3. Results and discussions

3.1. Morphology and structure

In order to determine the contents and profiles of Mo and C in the films, RBS analysis was performed and the spectrum was fitted [11] using the SIMNRA program as shown in Fig. 2. It can be observed that molybdenum is uniformly distributed in our sample. According to the simulated result, the thickness of the DLC film is about 1.98 μm and the transition layer of Mo film is 320 nm. The experimental value of total thickness obtained from section SEM image is 2.23 μm. The deviation between simulated and measured value is 3.14%. The carbon content of the as grown films increases