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Structural properties of hydrogenated Al-doped diamond-like carbon films fabricated by a hybrid plasma system

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ABSTRACT

Hydrogenated Al-doped diamond-like carbon films were prepared in a hybrid plasma system combines magnetron sputtering and anode layer ion source, which allows independent control of the incorporated-Al content and carbon film structure. In order to achieve gradual structure and property transition from substrate to DLC film, a functionally gradient interlayer Cr/CrC$_x$/Cr$_x$Al$_y$C was tailored deposited. The influence of methane flow rate on chemical composition, morphologies, and microstructure of the resultant films were studied. The residual stress, mechanical and tribological properties were investigated by using laser stress-tester, nano-indentation and ball-on-disc tribo-meter, respectively. The results suggested that the Al-DLC films have a characteristic of amorphous structure and the incorporated Al atoms were dissolved in the matrix without bonding with C atoms. A significant residual stress reduction was found in Al-doped DLC film compared with pure one (3.8 GPa). The Al-DLC film deposited at the optimum methane flow rate exhibited a unique combination of desirable properties, including moderate hardness, good adhesion strength, low friction coefficient and good wear resistance, which make it a promising candidate as protective films for engineering applications.

1. Introduction

Diamond-like carbon (DLC) films have found a wide range of industrial applications in bearings, drills, molds, artificial prosthetics and magnetic recording devices, due to their good combination of superior properties, such as high hardness, low friction coefficient, good wear resistance, biocompatibility and chemical inertness [1–3]. However, the main drawbacks of DLC films including high internal stress ranging from several gigapascals to 10 GPa and poor adhesion to the underlying substrates may cause a premature failure and delamination, drastically limiting their practical applications [4, 5]. Thus, the design and preparation of DLC films with desirable properties and low internal stress have attracted considerable attention in both fundamental research and engineering applications. Several approaches have been proposed to overcome the restrictions, for instance, doping with metal or nonmetal elements [6–8], tailoring graded interlayer [9, 10], growing the films with multilayer structure [11], post thermal annealing [12]. Among them, incorporation of additional metallic atoms into the carbon-based matrix has been demonstrated as being effective in releasing internal stress and improving the toughness of DLC films [6, 13–15]. It has been found that the chemical state of dopants has a significant influence on the final microstructure and properties of Me-doped DLC films. The weak-carbide-forming (WCF) metal atoms, including Cu [16], Al [17], Ag [18], etc., which are relatively inert to carbon or form very weak bonds with carbon when embedded in the amorphous carbon matrix. Previous studies have confirmed that metallic Al can relax the internal stress of DLC films more pronouncedly than that of strong-carbide-forming (SCF) metal such as W [7] and Ti [13, 19]. Furthermore, Wilhelmsson and his co-workers [20] found that alloying with Al atoms could reduce the friction coefficient by as much as 85% due to the improvement of ability to form a carbon-rich tribofilm.

Unfortunately, the incorporation of Al into the carbon-based matrix would inevitably deteriorate the hardness of DLC films due to the reduction in the sp^3 hybridization. Thus, an appropriate deposition technique to prepare Al-DLC films with desirable integrated properties and low internal stress is of great value in the application domain. There are several techniques for the preparation of metal-containing DLC films, including magnetron sputtering or arc evaporating a metallic target in the argon and hydrocarbon gas mixture atmosphere [14, 21, 22]. Anode layer ion source is a type of gridless ion gun that can be utilized for DLC films preparation at low deposition temperature by feeding carbon-containing gases. The main advantages of this technique

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are the simple and robust construction with maintenance-free operation and minimum wear of the cathodes [23]. Compared with direct current (DC) magnetron sputtering, the MF magnetron sputtering with much higher energy fluxes reaching the substrate can produce high quality films [24]. However, the Al-DLC films fabricated by using a hybrid plasma coating system, which combines middle frequency (MF) magnetron sputtering and anode layer ion source, are scarcely reported.

In this paper, hydrogenated Al-doped DLC films with tailored graded Cr/CrC$_x$/Cr$_x$Al$_y$C interlayer were synthesized by a hybrid plasma system composed of magnetron sputtering units and anode layer ion source. The effects of methane flow rate on the microstructure and properties of Al-DLC films were in-depth investigated. We correlate the observed changes in the tribological behaviors with the variations in microstructure, bonding environment, residual stress and mechanical properties.

2. Materials and methods

Hydrogenated Al-DLC films were prepared on n-type (100) silicon wafers and 304 stainless substrates by a hybrid plasma system, which composed of a DC magnetron sputtering Cr target, MF magnetron sputtering twin-Al targets and an anode layer linear ion source. The methane and argon were introduced simultaneously into the anode layer ion source to obtain hydrocarbon radicals. During the film deposition, the anode layer ion source was operating in low-voltage mode with a typical discharge current and voltage of 1.5 A and 300 V, respectively. Prior to loading into the chamber, the specimens were ultrasonically cleaned in acetone and ethanol for 20 min. The vacuum system was evacuated down to a base pressure of 4.0×10^{-3} Pa, and then the substrates were sputter-cleaned for 30 min by Ar$^+$ flux, which generated in the anode layer ion source to remove the residual contaminants. In order to enhance the bonding and adhesion strength, a functionally gradient Cr/CrC$_x$/Cr$_x$Al$_y$C interlayer was deposited beforehand. First, the substrate surface was ion bombarded with Cr species from the DC metallic Cr target at the operating current of 3 A. The applied negative bias voltage to the substrates was 800 V with processing time of 6 min. Then the DC deposition parameters for Cr target were maintained, while the bias voltage was decreased to −150 V to deposit a Cr layer for 5 min. Subsequently, methane was gradually introduced into the ion source to prepare CrC$_x$ layer at a flow rate changing from 0 to 20 cm^3/min. This process lasted 6 min. Then Cr$_x$Al$_y$C layer was prepared by gradually increasing the current of MF twin-Al targets (from 0 A to 3 A) and decreasing the current of Cr target (from 3 A to 0 A). This process lasted 8 min. Finally, the Al-DLC films were fabricated on top of the gradient interlayer under 100 cm^3/min Ar and varied methane gas flow rates (20 cm^3/min, 30 cm^3/min, 40 cm^3/min, 50 cm^3/min, 60 cm^3/min), at an optimum bias voltage of −150 V with a duty factor of 70%. The process pressure was maintained at 0.45 Pa via throttle valve. The MF magnetron sputtering Al-targets were operated at constant current of 3 A, and the deposition time was 120 min.

Surface morphologies of as-deposited films were characterized by field emission scanning electron microscope (FE-SEM, FEI Quanta-200). The compositions and chemical bonds of carbon and aluminum were performed on an Escalab 250Xi X-ray photoelectron spectroscope (XPS) operating with monochromated Al K$_\alpha$ irradiation at pass energy of 29.4 eV. Prior to acquiring the core level spectra samples were sputtered-cleaned in situ in the chamber for 2 min with 2 keV Ar$^+$ ion beam to remove oxide and contaminants. A built-in electron and ion neutralizers was used to compensate for surface charging. Raman spectroscope (Horiba Jobin Yvon, HR800) was employed to analyze the bonding structure of carbon atoms by using a 532 nm Ar$^+$ laser as the excitation source in the range of 500–2000 cm^{-1}. The microstructure was characterized by using a field emission transmission electron microscope (TEM, FEI Titan 200), where the accelerating voltage was 200 kV. The cross-section sample was prepared by using the focus ion beam technique (FIB, FEI Nanolab-450S).

The residual stress of as-deposited films was calculated by the Stoney equation. The curvatures of substrates before and after deposition process were determined by a laser stress-tester. Hardness and elastic modulus were measured by using a nano-indentation tester (CSM) with a Berkovich diamond tip, where the maximum indentation depth was less than 1/10 of the film thickness to minimize the soft substrate contribution. The adhesion strength was determined by a scratch tester, in which the load was progressively increased from 0 N to 100 N at the rate of 100 N/min. The tribological behaviors of the films were performed on a unidirectional rotating-type ball-on-disk tribo-meter (Bruker, UMT-3) under dry friction in ambient atmosphere with a relative humidity of 50 ± 2%. The counterpart was Si$_3$N$_4$ ceramic ball with a diameter of 4 mm, all frictional tests were performed under a load of 5 N with a sliding velocity of 0.2 m/s for 60 min. Subsequently, the wear tracks and wear scars formed on the counterfaces were characterized by using SEM and Raman spectroscopy.

3. Results and discussion

3.1. Chemical composition

Fig. 1 shows the variation of chemical concentrations as a function of methane flow rate. The C concentration increases monotonically from 53.9 to 95.6 at.%, while the Al and O concentration decrease as the methane flow rate increased from 20 cm^3/min to 60 cm^3/min. This trend can be explained by the fact that more CH$_4$ molecules were dissociated with the increase of methane flow rate. On the other hand, the Al targets were gradually covered with carbonaceous species, giving rise to the reduction in the amount of Al atoms sputtered from the metallic targets, which was referred to as “target poisoning”. A similar trend was reported by Zhang et al. [17] and Jiang et al. [25] who used magnetron sputtering metallic target in the argon and methane atmosphere.

Fig. 2 shows the high resolution XPS C 1s and Al 2p spectra of the Al-DLC films deposited at different methane flow rates. There is a major peak centered about 284.8 eV in all of the as-deposited films, which represents a typical binding energy of amorphous carbon. The C 1s spectra (Fig. 2b) were deconvoluted into three components centered at 284.3 eV, 285.2 eV and 286.5 eV, which corresponding to sp^2 carbon bond, sp^3 carbon bond and C—O bond, respectively. Besides, the peaks of aluminum carbide and aluminum oxycarbide, which have a binding energy of 281.5 eV and 282.5 eV, respectively, as reported in literature [13], were not found in the C 1s spectra. As shown in Fig. 2(c), the peak

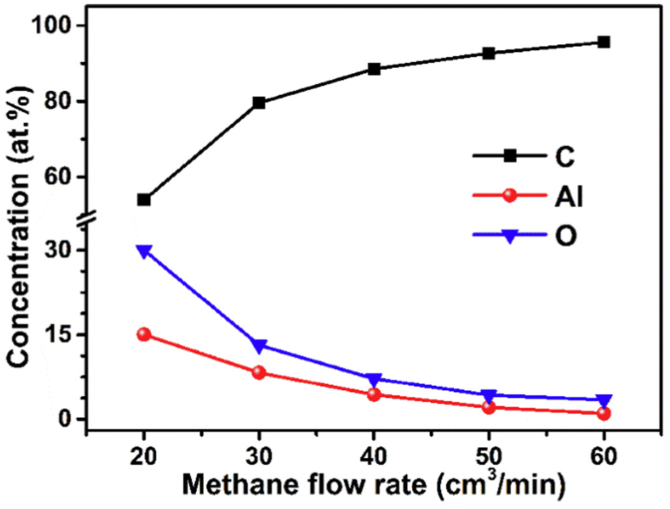

Fig. 1. The chemical composition of the films as a function of methane flow rate.