Surface & Coatings Technology 232 (2013) 575–581

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Effect of microstructure and mechanical properties difference between sub-layers on the performance of alternate hard and soft diamond-like carbon multilayer films

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ARTICLE INFO

Article history:
Received 27 March 2013
Accepted in revised form 8 June 2013
Available online 14 June 2013

Keywords:
Multilayer
Modulus ratio
Stress ratio
Toughness
Tribological properties

ABSTRACT

Alternate hard and soft diamond-like carbon (DLC) multilayer films with different modulus ratio and residual stress ratio between adjacent sub-layers were prepared by magnetron sputtering through alternating deposition bias. The microstructure, hardness and toughness of DLC films as well as their tribological properties under dry and water-lubricated sliding conditions were systematically studied in relation to the effects of modulus ratio and residual stress ratio between adjacent sub-layers. For multilayer DLC films with similar microstructure of adjacent sub-layers, the higher bias dominates the transformation from sp2 to sp3 carbon. As to multilayer DLC films with much different microstructure between adjacent sub-layers, the compact and ordered sub-layer structures formed under lower bias keeps growing even under higher deposition bias. Although multilayer strengthening effect is insignificant in multilayer DLC films, multilayer toughening effect is outstanding. Multilayer DLC films deposited at a substrate bias alternating between −120 and −160 V have the highest toughness which is almost double of that of monolayer DLC films, because the multilayer structure with low modulus ratio contributes to reduce the stress concentration in harder sub-layer thereby inhibiting crack initiation. Moreover, multilayer DLC films show better wear resistance than monolayer DLC films under both dry and water-lubricated sliding conditions. It was found that the higher toughness inhibited abrasive wear on the sliding steel counterface and contributed to the formation of transfer film.

1. Introduction

Multilayer structure hardening and toughening are significant in terms of the development of novel tough and stiff ceramic materials [1–4]. This is because the spatial variation of elastic modulus and the residual stresses in multilayer structures influence the driving force of crack tip thereby leading to changes in mechanical properties [4–6]. In fact, an effective crack stopping occurs in the soft layer of biological materials with an elastic modulus ratio of above 5 [3], and varying residual stress has much larger effects on the fracture toughness of materials than varying elastic modulus [4]. Particularly, multilayer structures can be constructed to increase the fracture toughness of ceramic materials by several times [4,7,8]. Actually, the fracture toughness mentioned above is usually measured according to ASTM standards in which a precrack is necessary [9]. Such techniques, however, are unsuitable for thin films. In most of the testing methods for thin films, there is no known precrack to start with. The measurements inevitably embed crack initiation, thus the results are not the same as those obtained in the determination of the classical "fracture toughness" [9–12]. Then a question arises whether those conclusions about bulk materials are suitable for the design of multilayer films. Although some research about multilayer films showed that multilayer structure was in favor of coating toughness and wear resistance [10–12], how to design tough and wearable films through constructing multilayer structure, and the effect of modulus ratio and stress ratio on multilayer films toughness and wear rate have not been studied systematically.

We pay special attention to multilayer DLC films, since their microstructure and mechanical properties can be well manipulated to vary in a wide range [13,14]. For example, the modulus ratio and stress ratio between soft and hard sub-layers of DLC multilayer films can be easily controlled without introduction of any other element or phase structure. This makes it feasible for DLC multilayer films to be readily adopted to search answer or countermeasure to the aforementioned question and challenge. Bearing this perspective in mind and noticing that previous studies on DLC multilayer structures highlight the effects of thickness or/and ratio of soft and hard layers on the hardness, internal stress and tribological properties [15–19]. In the previous work, it has been found that bias-alternating deposition results in high quality multilayer DLC coatings with low residual stress and high adhesion strength [20]. In this research, we focus on the effect of modulus ratio

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http://dx.doi.org/10.1016/j.surfcoat.2013.06.030

and stress ratio of soft and hard layers on the microstructure and mechanical properties of DLC multilayer films.

This paper reports the fabrication of a series of DLC multilayer films as well as their microstructure, mechanical properties and tribological properties under dry sliding and water-lubricated conditions. In particular, DLC multilayer films with fixed hard sub-layer and soft sub-layer whose hardness can be controlled by changing substrate bias are fabricated so as to get multilayer DLC films with different modulus ratio and stress ratio of adjacent sub-layers. Such a strategy aims to study, hopefully, to help to study the effect of microstructure and mechanical properties difference between sub-layers on the performance of alternate hard and soft DLC multilayer films.

2. Experimental

2.1. Preparation of DLC films

DLC single-layer and multilayer films were deposited on single crystal silicon substrates with an E303A magnetron sputtering system (Penta Vacuum, Singapore; target: pure graphite with a purity of 99.999% (mass fraction)). The details about the deposition facility and procedures are available elsewhere [20]. Three series of films were deposited: (1) 10 nm/layer × 30 layers; (2) 5 nm/layer × 60 layers with substrate bias alternating between −40 V and −160 V, −80 V and −160 V, and −120 V and −160 V at room temperature; and (3) monolayer deposition under the same conditions except at constant bias of −40 V, −80 V, −120 V, and −160 V as comparison. The power density at the graphite target was kept at 12.3 W/cm^2.

2.2. Characterization of DLC films

The cross-sectional microstructure and chemical bonding of various as-deposited DLC films were analyzed with a JEM-2010 transmission electron microscope (TEM, Jeol Corporation, Japan) and a Renishaw Raman Spectroscope (RM1000) with the 633 nm line of a He–Ne laser..

Coating hardness measurements were conducted with a Nanoindenter (XP, MTS, Inc., USA) with a Berkovich diamond indenter and determined by continuous stiffness measurement technique. A total of six indentations with a spacing of about 30 μm were employed on the surface of each DLC film sample; and the average of the six repeated measurements was calculated as the final hardness value.

Based on Michel model [21], the toughness of as-deposited DLC films can be calculated as

$$K_{ic} = \left(\frac{E}{(1-V_f^2)L}\frac{\Delta U}{t}\right)^{1/2}. \quad (1)$$

Where E is the elastic modulus of thin film, V_f is the Poisson's ratio of the film, L is the length of cracks on the film surface (the cracks were produced also by the Berkovich diamond indenter of the XP nanoindenter), t is the thickness of the film, and ΔU is the strain energy difference before and after cracking ($\Delta U = U - U_s$; U is the total energy during chipping stage, and U_s is the energy dissipated during elastic and plastic deformations of Si substrate during loading). In terms of the Michel model, there is an assumption that the deformation behavior of single crystal Si substrate is almost the same whether there is a film or not. The magnitude of the residual stresses was calculated from the change in radius of curvature of silicon substrate measured by a Tencor laser scanner before and after deposition which has been explained in details in reference [20].

A reciprocal ball-on-disc tribo-meter (UMT-2, CETR, USA) was used to evaluate the tribological behavior of DLC films under both dry and water-lubricated sliding conditions. Before each friction and wear test was commenced, the counterpart stainless steel balls (diameter: 4 mm) were cleaned with acetone in an ultrasonic bath. All the sliding friction and wear tests were conducted under a load of 4 N, a frequency of 2 Hz, and a reciprocating amplitude of 5 mm at a room temperature of 25 °C and a relative humidity of 45% ~ 60%. Volume wear rate is calculated as $K = V / SF$, where V is the wear volume loss of DLC films at a test duration of 30 min, S is the total sliding distance, and F is the normal load. A surface profiler (2206B, HMCT, China) was employed to obtain the wear track profiles of each tested DLC film sample, and then the wear volume loss was determined after the dimensions of the wear track profiles were considered. Four repeated friction and wear tests were conducted under identical conditions for each DLC film sample, then the average wear rate of the four repeated tests was calculated. Here the coefficient of friction is the average value over the steady-state of the four repeated tests. Moreover, a JSM-5600 scanning electron microscope (SEM; Joel, Japan) was performed to observe the wear track morphology of various DLC films and the wear scar morphology of counterpart steel balls.

3. Results and discussion

3.1. Bonding structure and microstructure

Raman spectroscopy is widely used to analyze the bonding structure of DLC films, and it allows correlating well the bonding structure and phase evolution of DLC films from graphite to amorphous structure with the position of G peak (~1580 cm^{-1}) and D peak (~1350 cm^{-1}), the intensity ratio of D and G peaks (I_D/I_G), and the full width at half maximum (FWHM) of the D and G peaks [22,23]. Usually, G peak FWHM not only gives information on structure disorder arising from the bond angle and bond length distortions but also is directly proportional to the sp3 content [23]. Raman data for various DLC films are available in our previous work [20]. Herein, we focus on the correlation between the microstructure and Raman data of DLC films. The G peak FWHM of monolayer DLC films and multilayer DLC films versus substrate bias is plotted in Fig. 1, and their high-resolution TEM (denoted as HRTEM) images of cross-sections are presented in Fig. 2. It can be seen that the G peak FWHM of monolayer DLC films increases with increasing substrate bias from −40 V to −160 V. Particularly, the monolayer DLC film deposited under a low substrate bias has a kind of turbostratic structure which is typical carbon structure builded up by imperfect graphenic lamellae with enlarged interplanar spacing [13]. From Fig. 2a, it can be seen that

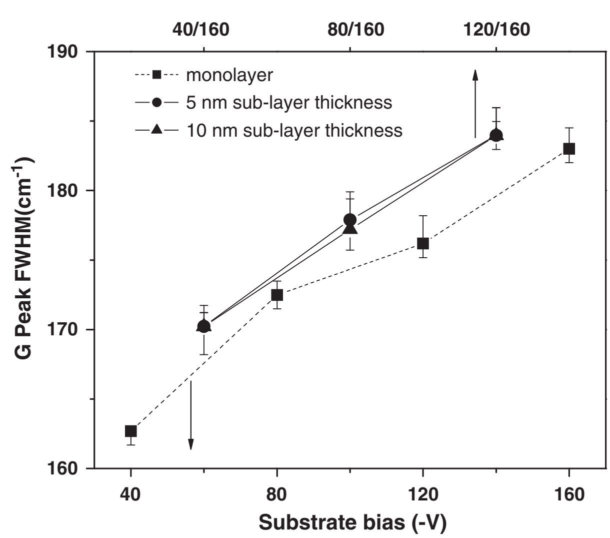

Fig. 1. G peak FWHM of monolayer DLC films and multilayer DLC films deposited under different biases.