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Three-layered sandwich structured carbon film prepared by sputtering and ion/electron/ion alternative irradiation

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ABSTRACT

The electron irradiated carbon film based on electron cyclotron resonance (ECR) sputtering technology has been proved to have both high conductivity and paramagnetism. However, the relatively low hardness, wear life and high surface roughness value limit its application in Micro-electromechanical Systems (MEMS). To improve these properties, the sandwich structured carbon films with different modulation ratios were introduced on silicon (100) wafers by alternative irradiation (ion/electron/ion) technique in ECR sputtering system. The three-layered nanostructure of films was measured with a transmission electron microscopy (TEM). The surface roughness of the film can be controlled to 0.19 nm according to the measurement of atomic force microscope (AFM). The unique characteristics of electron irradiated layer remained stable after irradiation through the analyzing of Raman spectroscopy. The mechanical properties (including hardness, elastic modulus, fracture behavior) and wear life were improved significantly due to the sandwich structure. The results showed that the sandwich structured carbon film is a kind of functional material equipped with enhanced mechanical and tribological properties.

1. Introduction

With the rapid development of nanotechnology, nano functional materials are required to have both good tribological and mechanical properties to cope with more complex application situations. Multilayer coating technique is one way to achieve the goal. Nano multilayer film is typically artificial materials composed of alternating layers with different materials. The thickness of each layer can be from several to hundreds of nanometers. The multilayer film system can overcome the disadvantages of monolithic film and has much better comprehensive properties [1–3]. Wang et al. prepared electron irradiated monolithic carbon film by electron cyclotron resonance (ECR) sputtering technique, which has been proved to have relatively high conductivity [4] and paramagnetism [5]. However, it was also found that this kind of film had the limitations of relatively low wear resistance, hardness and poor bonding strength with substrate, which means that it would suffer a higher risk in deformation, spalling and abrasion when facing a contact or friction in MEMS, leading to a change in conductive property [6] or magnetic degradation [7]. In order to improve the tribological and mechanical properties of the electron irradiated film, we constructed a three-layer sandwich structured carbon film by using multilayer coating technique and assembling the electron irradiated film with relatively hard ion irradiated carbon film together. The ion irradiated layer lying between substrate and electron irradiated layer could serve as undercoat layer to enhance the bonding strength with the substrate.

Several studies about the properties of multilayer carbon films have been reported. Han et al. explored hardness, elastic modulus and stress trend of graded multilayer tetrahedral amorphous carbon film [8]. Xu et al. investigated the influence of modulation ratio on composition, hardness, residual stress, adhesion property and tribological characterization in four-layer carbon film [9]. Liu et al. developed a finite element model of multilayer carbon film with different layer number to analyze stress distributions induced by wear particles [10]. However, the multilayer carbon film in the aforementioned study was simply served as protecting films and seldom considered as functional materials. In this paper, we proposed an ECR ion/electron/ion alternating irradiation technique for fabricating a multilayer functional material, and a sandwich structured carbon film with hard/soft/hard layers was fabricated to evaluate the technique. The evaluating experiments using TEM, AFM and Raman spectra were carried out to analyze the structure, surface roughness and chemical composition respectively. The tests on hardness, elastic modulus, residual stress, fracture behavior and tribological characterization

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between monolithic and sandwich structured carbon film were also conducted to for exploring a novel functional material.

2. Experiment

2.1. Film preparation

The sandwich structured carbon films were deposited on Si (100) (20 × 20 × 0.5 mm) with ECR-sputtering technique [11]. Prior to the deposition, the chamber was pumped to a background pressure of 4.10×10^{-4} Pa and high purity argon was introduced into the chamber as the working gas with a pressure of 4.00×10^{-2} Pa. During the deposition, a DC bias voltage of −300 V was applied to the carbon target. The monolithic electron irradiated carbon film was fabricated at a substrate bias voltage of +50 V under the Mirror Confinement ECR (MCECR) mode [4]; while the ion irradiated film was deposited at a voltage of −5 V under the Divergent ECR (DECR) mode. All of the samples were prepared at room temperature. However, the substrate temperature of electron irradiated film raised up to 200 °C, while that of ion irradiated film almost remained the same during sputtering. The process of ECR ion/electron/ion irradiation is illustrated in Fig. 1. Five sandwich structured carbon films were obtained with different modulation ratios (deposition time ratio of an ion irradiated layer to an electron irradiated layer). The total deposition time for one film was 1500 s. Due to the different deposition rates between ion and electron irradiated layers and the possibility of ion etching, the total thickness of these films were not exactly the same. The detailed experimental parameters are shown in Table 1.

2.2. Characterization of films

The nanostructures of sandwich structured carbon films were observed using TEM (JEM-2100) with the electron acceleration voltage of 200 kV. TEM specimens for the cross-sectional view were prepared by mechanical polishing followed by argon-ion beam milling to a thickness appropriate for observation. The surface roughness measurement was carried out by using an AFM (Bruker Innova). The chemical composition was analyzed by Raman spectra (Horiba HR800) with a laser wavelength of 514 nm, and spectra region between 1100 and 3500 cm^{-1}. The conductivity was measured by the four-point probe method at room temperature.

The elastic modulus and hardness of the different structured carbon films were measured by a nanoindenter (Hysitron TI-900) and calculated by Oliver–Pharr method. In the test, a Berkovich diamond indenter with a tip radius of 200 nm and the maximum load of 1 mN were used. A pre-test on quartz standard sample was done to calibrate the equipment. The value of the elastic modulus and hardness of the samples were given by averaging three different measurement results. The radius of curvature of the substrate was measured using a stylus profilometer (Ambios XP-2), and the residual stress was calculated through Stoney's formula [12].

Table 1
The experimental parameters of carbon films.

Sample name	Deposition time of ion irradiated layer (bias = −5 V)	Deposition time of electron irradiated layer (bias = +50 V)	Modulation ratio (ion: electron irradiated layer)	Thickness
M0-E	–	1500 s	–	150 nm
M1	500 s	500 s	1:1	140 nm
M2	600 s	300 s	2:1	125 nm
M3	667 s	167 s	4:1	110 nm
M4	700 s	100 s	7:1	105 nm
M5	720 s	60 s	12:1	102 nm
M0-I	1500 s	–	–	100 nm

$$\sigma_f = \frac{E_s d_s^2}{6(1-\nu_s)d_f}\left(\frac{1}{R_{post}} - \frac{1}{R_{pre}}\right)$$

where E_s, ν_s and d_s were the elastic modulus, Poisson's ratio and thickness of the Si (100) substrate, respectively. R_{pre} and R_{post} were the curvature radii of substrate before and after deposition. Fracture behavior was tested using the nanoindenter (Hysitron TI-900) as well. A cube diamond indenter with a tip radius of 50 nm and the maximum load of 10 mN were used to ensure the happening of fracture and compare with single amorphous carbon film [13]. The loading/unloading rate was 10 mN/min and holding time at maximum load was 5 s. The tribological experiments of the carbon films were operated on a ball-on-disk tribometer. The test conditions are at room temperature (23 °C) and a relative humidity about 40%. A Si_3N_4 ball was used for the frictional tests. The normal load was 1 N and sliding velocity was 19 mm/s with a frictional circle radius of 1.4 mm.

3. Experimental results and discussions

3.1. Nanostructures

Fig. 2 illustrates the cross-sectional view of two sandwich structured carbon films fabricated by ECR ion/electron/ion irradiation technique.

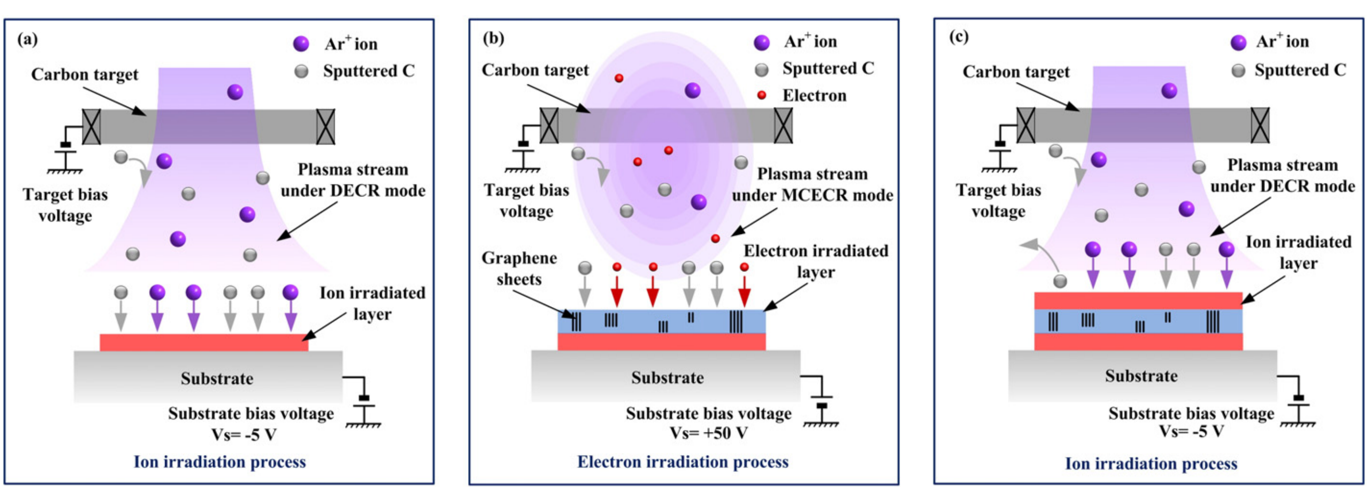

Fig. 1. Schematic illustration of the experimental design for ECR ion/electron/ion irradiation process. (a) Ion irradiation process of the first layer in sandwich structured carbon film. (b) Electron irradiation process of the second layer in sandwich structured carbon film. (c) Ion irradiation process of the third layer in sandwich structured carbon film.