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Silicon and aluminum doping effects on the microstructure and properties of polymeric amorphous carbon films

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ABSTRACT

Polymeric amorphous carbon films were prepared by radio frequency (R.F. 13.56 MHz) magnetron sputtering deposition. The microstructure evolution of the deposited polymeric films induced by silicon (Si) and aluminum(Al) doping were scrutinized through infrared spectroscopy, multi-wavelength Raman spectroscopy, scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM). The comparative results show that Si doping can enhance polymerization and Al doping results in an increase in the ordered carbon clusters. Si and Al co-doping into polymeric films leads to the formation of an unusual dual nanostructure consisting of cross-linked polymer-like hydrocarbon chains and fullerene-like carbon clusters. The super-high elasticity and super-low friction coefficients (<0.002) under a high vacuum were obtained through Si and Al co-doping into the films. Unconventionally, the co-doped polymeric films exhibited a superior wear resistance even though they were very soft. The relationship between the microstructure and properties of the polymeric amorphous carbon films with different elements doping are also discussed in detail.

1. Introduction

Hydrogenated amorphous carbon (a-C:H) films are of interest to carbon material researchers, due to their beneficial physical and chemical properties, such as superior mechanical properties, high optical transmittance, excellent wear resistance, and outstanding chemical inertness [1,2]. These films consist of a mixture of sp^2 and sp^3 hybridized carbon phases with different levels of hydrogen. The properties of a-C:H films are mainly determined by the fraction ratio of sp^3 to sp^2 carbon phases. Films with a high fraction of the sp^3 (C—C bonding, not C—H bonding) phase, such as tetrahedral (ta-C:H) and diamond like (DLCH)hydrogenated amorphous carbon films, usually exhibit a very high hardness and elastic modulus. Also, the properties of a-C:H films, especially the tribological behaviors under a vacuum or inert atmosphere are significantly influenced by the hydrogen content. Erdemir [3] found that a-C:H films with high content of hydrogen performed at a super-low friction coefficient of 0.001 with superior wear resistance in an inert-gas environment, while hydrogen-free amorphous carbon films had values as high as 0.6 and were worn out in a short time. The excellent tribological properties of a-C:H films under a vacuum or inert atmosphere make them good candidates for lubrication materials under a vacuum or in space environments. However, the main limitation of a-C:H films is a high internal stress causing delamination and limiting the film thicknesses [1]. Fortunately, the element doping can offer an effective approach to break the limitations. For example, silicon (Si) is most frequently doped into the amorphous carbon films due to its effective enhancement of thermal stability; better frictional properties can be achieved through its doping [4,5]. Aluminum (Al) has been regarded as one of the most effective elements for relaxing internal stress of amorphous carbon films [6]. Also, it can improve the segregation of graphitic carbon from the amorphous carbon structure and lead to a low friction on the contact interface [7]. In addition, the concept of co-doping or multiple doping has also been proposed to develop nanostructural or nanocomposite amorphous carbon films [8]. The mixture of the various phases induced by the co-doping might achieve some synergic effects on the nanostructure and properties of the nanocomposite films [7] our previous studies found that the co-doped Si and Al synergistically regulated the chemical structure, mechanical and tribological properties of the hard a-C:H films [9]. In this paper, the synergic effects of Si and Al on the soft a-C:H films will be scrutinized.

Polymeric or polymer-like carbon films, a special kind of soft a-C:H film consisting of abundant polymer-like hydrocarbon chains [10], exhibit a wide optical band gap with a strong photolu-

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minescence in the visible range at room temperature. Thus a lot of interests have been paid to such kinds of amorphous carbon films because of their electronic and optical properties [11]. Furthermore, Donnet et al. [12] reported that the tribo-induced polymer-like hydrocarbon layers on the contact interface played a critical role in the super-low friction behavior of the a-C:H films under a vacuum. This means that the polymer-like amorphous carbon films prepared by physical or chemical vapor deposition should also exhibit the super-low friction behavior under the same environments. Unfortunately, because of their low hardness, the tribological behaviors of this kind of amorphous carbon films have received less attention compared with the hard DLCH and ta-C:H films; especially the effects of element doping on the microstructure and tribological properties have been rarely reported, to our knowledge.

In the view of above mechanism and the previous enlightening studies, we prepared polymeric amorphous carbon films with different doping elements by magnetron sputtering deposition. The evolution of the microstructure induced by successive introduction of Si and Al into the films was studied for the first time. The mechanical properties and frictional behaviors of the deposited polymeric amorphous carbon films under a high vacuum were comparatively investigated. The effects of Si and Al doping on the nanostructure, mechanical and tribological properties of polymeric amorphous carbon films were illuminated.

2. Experimental details

2.1. Film deposition

Polymeric amorphous carbon films were deposited on n-type Si (100) substrates by R.F (COMDEL, Gloucester, MA, USA) magnetron sputtering in an argon (Ar) and methane (CH_4) mixture plasma. The flow rates of CH_4 and Ar were controlled at 27 SCCM (SCCM denotes cubic centimeter per minute at STP) and 40 SCCM, respectively. Three kinds of targets were used to deposit polymeric amorphous carbon films with different doped elements. Pure graphite (99.99 wt.%) and pure silicon (99.999 wt.%) targets were sputtered to deposit pure (a-C:H) and Si doped (Si/a-C:H) polymeric amorphous carbon films, respectively. A composite target consisting of silicon (99.999 wt.%) and aluminum (99.5 wt.%) with 6:1 area ratio was sputtered to deposit Si-Al co-doped polymeric amorphous carbon films [(Si-Al)/(a-C:H)]. The R.F. power and sputtering pressure were controlled at 700 W and about 1.2 Pa, respectively. Deposition time of the films was fixed at 90 min. The base pressure of the deposition chamber was evacuated to about 4×10^{-4} Pa. Before the deposition beginning, the substrates were treated by the following steps: (i) ultrasonically cleaned in acetone and alcohol for 10 min, respectively; (ii) cleaned using an Ar ion bombardment at a pressure of 1.2 Pa and a bias voltage of -1000 V with a 70% duty factor for 10 min to remove some adhering impurities on the substrates; (iii) a titanium interlayer with about 300 nm was deposited through middle frequency magnetron sputtering the pure titanium target to improve the adhesion of the films. The distance between the substrate and target was controlled at about 9.0 cm. Neither a negative bias voltage nor additional heat was applied to the substrates during the deposition of the films. The substrate temperature was not higher than 90 °C. The duration of the film deposition was 90 min. The deposition set-up has been shown in a previous paper [13].

2.2. Film characterizations

A fractured cross section of the films was surveyed by field emission scanning electron microscopy (FESEM, JSM 6701F) and high resolution transmission electron microscopy (HRTEM) at 200 kV (Tecnai G2 F20, FEI). The thickness of the films was measured according to the scale of the FESEM observation with a magnification of 10,000. Six replicate measurements were made at different position for each sample. The surface morphology was observed by an atomic force microscope (AFM, SPA-400, NSK) with a silicon probe under tapping mode, and the scanning area was set at $5 \times 5\ \mu m^2$. The samples for HRTEM observation were prepared by mechanical polishing and then Ar ion milling (Gatan 691) at a small angle with respect to the milled surface. Infrared spectra(IR) of the films were obtained under attenuated total reflectance mode in air (Thermo Fisher Scientific, Nicolet IS10). The substrate background of all the IR spectra of deposited films was subtracted by pre-scanning the bare wafer. It is useful to probe the a-C:H films at visible and UV excitations and the clustering of sp^2 carbon sites can be deduced, especially when the films contained high amount of hydrogen [14]. The Raman spectra were acquired on a HR800 Raman microscope with excitation wavelengths of 532 nm and 325 nm and a laser power of 0.1 mW. The composition and binding energy of the atoms in the films were analyzed by an X-ray photoelectron spectroscope (XPS, PHI- 5702). The hardness and elastic modulus of the films were investigated by a nano-indenter (TI950 Tribo-Indenter, Hysitron). The set-up was calibrated using fresh Si(100) and fused silica as references before the indentation tests. The depth of the indentation was controlled to 10% of the film thickness to exclude the influence of the substrates. The elastic recovery rate (W_e) of the films was calculated through Eq. (1), where $d_{\max}$ and d_{res} are the maximum and residual displacement, respectively.

$$W_e = \frac{(d_{max} - d_{res})}{d_{max}} \quad (1)$$

The frictional behavior of the samples was evaluated on a vacuum tribo-meter using the rotational ball-on-disc mode. Tribological tests were finished under a vacuum of 4×10^{-4} Pa at room temperature. The rotational speed was 500 rev min^{-1}, and the rotational radius was 6.0 mm, and sliding cycle was controlled at 15,000. The counter face was a standard AISI 52100 steel ball with 3 mm in diameter. The normal load was 2.0 N, corresponding to a theoretical initial Hertzian contact pressure of 1.0 GPa. The morphology of transfer layers on counter face were observed by SEM (JSM-5600). The wear tracks were characterized by optical microscopy. The wear rate (unit: mm^3/N m) was derived from the wear volume of the wear tracks determined by the non-contact method on the Micro XAM-3D Surface Profile(ADE Phase Shift, USA), as proposed in Ref. [9].

3. Results and discussion

3.1. Chemical composition and microstructure

The chemical composition, thickness and root mean square surface roughness (RMS) of the deposited films are summarized in Table 1. As the sputtering target changed, the composition of the films accordingly varied as expected. Oxygen was detected among all of the polymeric amorphous carbon films due to its surface adsorption from the air. However, the oxygen content of the (Si-Al)/a-C:H films was about twice that of the pure and Si doped polymeric films, which may be the result of the introduction of Al; this naturally leads to an increase in the affinity of oxygen because of its high reaction activity with oxygen. Furthermore, the increase in the surface roughness of the Si-Al co-doped films should also be in partly responsible for the increase in the oxygen content detected by the XPS, as the high surface area may lead to its increased adsorption from the air.

The cross sectional morphologies of the films surveyed by FESEM and HRTEM are shown in Fig. 1(a–f). All the films were