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Microstructure, mechanical and tribological properties of Si and Al co-doped hydrogenated amorphous carbon films deposited at various bias voltages

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ABSTRACT

Hydrogenated amorphous carbon films containing Si and Al (a-C:H/(Si, Al)) were deposited on Si(100) substrates at different negative bias voltages, by radio frequency (RF, 13.56 MHz) magnetron sputtering. The chemical composition and structure were detected by means of X-ray photoelectron spectroscopy (XPS) and Raman spectra, respectively. It was found from the results of Raman spectra that the film deposited at zero negative bias voltage was highly hydrogenated, but significant graphitization happened to the films when high bias voltages were applied. The results of atomic force microscope (AFM) showed that the films deposited at moderate negative bias voltage had ultra-smooth surface. The mechanical and tribological properties of the films were measured by nano-indentation test and tribo-meter in ball-on-disk mode, respectively. It was revealed that the negative bias voltage had great impacts on the mechanical properties of the films. The tribological properties of the films were significantly improved when bias voltages were applied on substrates. Particularly, the film deposited at −200 V performed a super-low friction behavior (0.0085) and long wear life ($>10^5$ revolutions) in ambient air under high Hertz contact stress (as high as 1.6 GPa) though it showed a relatively low hardness.

1. Introduction

In recent years, hydrogenated diamond-like carbon or a-C:H films have attracted extensive attention due to its superior physical, mechanical, and tribological properties [1]. Numerous techniques have been developed to prepare a-C:H films, for instance, ion beam sputtering or deposition (IBD) [2], filtered cathodic vacuum arc (FCVA) [3,4], pulsed laser deposition (PLD) [5,6], radio frequency (RF) plasma enhanced chemical vapor deposition (RF-PECVD) [7–9], and unbalance magnetron sputtering [10]. Among above mentioned techniques, the magnetron sputtering is a technique capable of depositing thin films from a wide variety of materials onto various substrate shapes and sizes [11] and is the most common industrial process for the deposition of DLC films [12,13]. Compared to direct current (DC) magnetron sputtering, radio frequency (RF) magnetron sputtering is independent of the conductivity of sputtering target, thus the RF magnetron sputtering system is more powerful to deposit doped amorphous carbon films by sputtering a poor conductive target. Besides, the RF magnetron sputtering can provide higher percentage of ionized particles in the vacuum chamber, which is in favor of reactive sputtering [14].

Technically, to remove the intrinsic limitations such as high inner stress, poor adhesion to some substrates and low toughness of a-C:H films as protective overcoats or wear resistance coatings, metal or nonmetal elements were incorporated into carbon matrix. There have been many reports that mechanical and tribological properties of a-C:H films have been greatly improved through introducing other elements (Si, Al, Ti, Cr etc.). However, a stable super-low friction has rarely been achieved in ambient air by introducing a single element. Then two or more elements incorporation may be taken into account due to some synergistic effect. As a matter of fact, the finding of super-low friction of titanium/silicon co-doped a-C:H film lends a support to such consideration [15]. Especially, it was reported that the humidity sensitivity of friction coefficient can be suppressed by incorporating Si into a-C:H films [16], and Al was one of the most effective elements in relaxing stress of a-C:H films [17]. Hence, in our previous work, a-C:H/(Si, Al) films were deposited through RF magnetron sputtering to explore the joint effects of Si and Al on structure, mechanical and frictional properties of the a-C:H films, and a super-low friction state was exhibited [18]. Normally, besides gas source, the deposition parameters like negative bias voltage and temperature of substrate could also significantly affect the microstructure and properties of a-C:H films.

Accordingly, in our present study, we deposited a-C:H/(Si, Al) films at various negative bias voltages. The effect of negative bias voltage on the microstructure, mechanical and tribological properties was discussed.

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2. Experimental details

The a-C:H/(Si, Al) films were deposited on n-type Si(100) using a composite target consisted of silicon (99.999 wt.%) and aluminum (≥99.5 wt.%) with area ratio of 6/1 in argon (Ar, 99.99%) and methane (CH_4, 99.99%) mixture plasma. The experimental setup can be found in Ref [19]. The RF power (13.56 MHz, COMDEL, Gloucester, MA, USA) was controlled to 700 W. Different negative bias voltages of −400 V, −300 V, −200 V, −100 V, and 0 V were applied to the substrates, accordingly denoted to Samples 1–5. The power of negative bias voltage was 40 kHz frequency and duty cycle of 70%. Other sample preparation details can be found in Ref [18].

The film thickness was measured by a surface profilometer. An atomic force microscope (AFM, SPM-Nano IIIa) was employed to scrutinize surface morphologies and root-mean-square (RMS) roughness of the films. The size of detected area is $2 \times 2\ \mu m^2$. The compositions of the films were analyzed by a PHI-5702 X-ray photoelectron spectroscope (XPS) with monochromatic Al Kα radiation at pass energy of 29.4 eV. The residual pressure of the system was lower than 3×10^{-8} Torr. Raman spectra were obtained on a HR800 Raman microscope instrument, with 532 nm Ar ion laser and a resolution of 1 cm^{-1}. The peak deconvolution of Raman spectra was done using a Gaussian function. The nano-indentation tests were done on Nano-test 600 (Micro Materials Ltd., UK) with a Berkovich diamond tip. The depth of indentation was about 10% of the film thickness in order to exclude the influence of substrates. Five replicate indentations were made for each sample, and then the hardness was calculated from the load–unloading curves. The error bars were calculated from the standard deviation of the five indentations.

UMT-2MT tribometer (Center for Tribology, Inc., USA) was used to evaluate dry-sliding frictional behavior in ball-on-disk mode in ambient air. The specific tribo-test parameters can be found in Table 1. Wear tracks were characterized by scanning electron microscope (JSM-5600) and HR800 Raman spectroscopy, respectively. The wear volume of wear tracks was measured using non-contact method on Micro XAM-3D Surface Profile. Then wear rate was acquired from the wear volume divided by the sliding distance and applied load.

3. Results and discussion

3.1. Compositions and thickness

The composition of samples was detected by XPS. The elemental concentrations of the samples were nearly independent of the negative bias voltage, as given in Fig. 1(a). The atomic percentages of C, O, Si and Al in the films were 90.4–93.4%, 4.1–6.8%, 1.4–1.8% and 0.3–0.9%, respectively. The fluctuations of the elemental compositions were relatively slight. However, as shown in Fig. 1(b), the film thickness decreased monotonously with the increase of the negative bias voltage. The films deposited at higher negative bias voltage were thinner. This kind of trend of film thickness can be attributed to ion energy which correlates highly to the negative bias voltage and plays an important role in deposition of a-C:H films [20]. The ion energy will be enhanced as negative bias voltage increases. Accordingly, the re-sputtering or ion etch is stronger [21,22], which make films dense but reduce its thickness.

Table 1
The parameters of tribo-tests.

Contact load (N)	2.0
Sliding revolution	1.8×10^4
Hertz contact stress (GPa)	~1.0
Relative humidity	30–40%
Sliding velocity (m/s)	0.10
Counterface	Stainless steel ball (AISI 52 100), Φ = 3 mm, HRC = 62, Ra = 0.02 μm

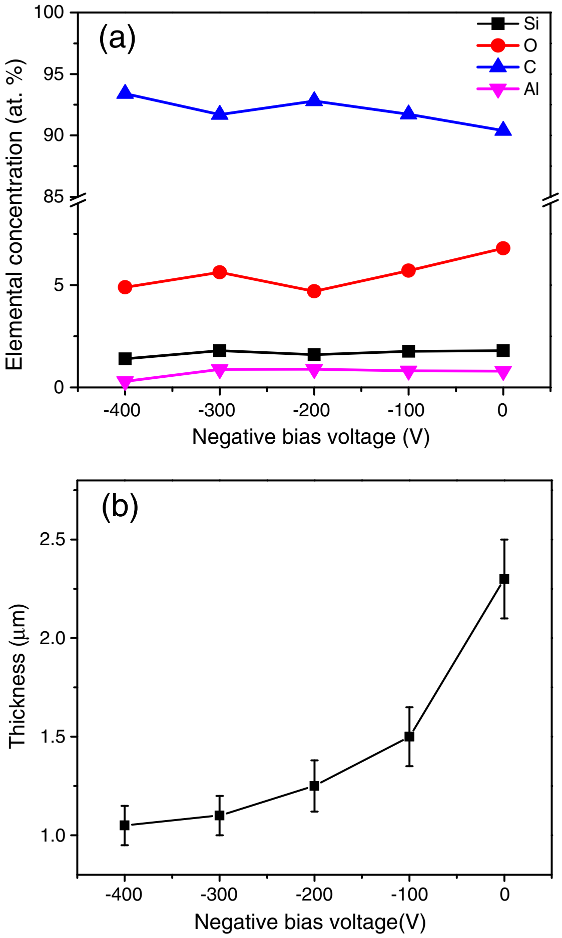

Fig. 1. The compositions (a) and thickness (b) of the films as a function of negative bias voltage.

3.2. Surface morphology

AFM images and the RMS surface roughness of the films deposited at various negative bias voltages are shown in Fig. 2(a)–(f). Unlike many previous researches which reported a monotonously change of surface roughness of amorphous carbon films with the increase of bias voltage [22–24], the RMS roughness of our films had a minimum value of 0.24 nm at −200 V bias voltage. To our knowledge, both surface diffusion of adatoms [25] and etching or erosions of energetic ions have impacts on smoothening of growing film surface [26]. Without collision of energetic particles, the surface diffusion is mainly driven by thermal energy. During room temperature deposition processes, the surface temperature of the growing films is not high enough to conquer the surface diffusion barrier, thus the surface diffusion should be very weak at 0 V bias voltage and should be ignored [27]. Correspondingly, surface diffusion could not alleviate the high-speed local adatoms accumulation. As a result, the surface RMS roughness of the film deposited at the bias voltage of 0 V was very high. On the other hand, when moderate negative bias voltages were applied, the surface RMS roughness of the films drastically decreased, which should be attributed to the etching of energetic ions [27]. However, the energetic ions, like a double-edged sword, would over-etch the growing film surface [2,28]. Therefore, a rough surface would grow if a too high bias voltage were applied.

3.3. Raman spectra

The Raman spectrum has been extensively employed to survey the structure information of a-C:H films since any mixture of sp^3, sp^2 and