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Enhancement of mechanical, tribological and morphological properties of nitrogenated diamond-like carbon films by gradient nitrogen doping

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ABSTRACT

Diamond-like carbon (DLC) films with gradient nitrogen (N) doping were synthesized by direct-current (DC) magnetron sputtering method. The effects of N doping on composition, adhesion, mechanical, tribological and morphological properties were investigated by Raman spectra, nano-scratch tester, nano-indenter and atomic force microscopy (AFM). The results of nano-scratch tester showed that the adhesion of DLC film was enhanced due to N introduction. The results of AFM, nano-scratch tester and nano-indenter showed that the doping method of gradient increased N component had a significant improvement in surface roughness and mechanical properties compared with the conventional N doping method. The gradient N doping (N^G-DLC) films also exhibited better tribological properties compared to conventional N doping (N^C-DLC) film. The adhesion and roughness were well achieved and improved simultaneously by utilizing a gradient N-doped deposition method for the first time. The relationship between tribological and mechanical properties was deduced and demonstrated. A model based on wave superposition theorem was built to interpret the relationship between surface roughness and N concentration during the deposition. The simulation results showed great agreement with the experimental results.

1. Introduction

DLC films with exceptionally mechanical and tribological properties have been used in a wide range of engineering applications, such as optical windows, biomedical coatings, magnetic storage disks [1–5]. However, unprocessed DLC films are restricted to be used due to some unsolved problems, such as poor adhesion and high residual stress. Recently, enhanced adhesion [6,7] and tribological properties [8] were observed in nitrogenated diamond-like carbon (N-DLC) films, which also showed the enhanced conductivity, corrosion resistance and excellent cytocompatibility (cell-compatibility) properties with some potential functionalities [7,9–10]. N-DLC films due to the excellent properties have attracted great attention [10]. The deterioration of mechanical properties and surface roughness were always found in N-DLC films due to N incorporation [8,11]. With the incorporated N content increase, the film performed better adhesion property, but higher surface roughness and a lower deposition rate [12].

At the first glance, it seems hard to combine these contrary properties. However, gradient structure has been utilized by many researchers to improve the overall performance of films. Liu et al. introduced thickness-gradient films to fabricate stretchable strain sensors, then the seemingly contrary properties of brittleness and stretchability were coupled together [13]. Yu et al. reported that elasticity-gradient polydimethylsiloxane (PDMS) substrates can be beneficial for a wide range of technological applications [14]. Roy et al. reported a method for creating a gradient topography surface on an elastomeric thin film to make it implementable without any specialized fabrication facility and is attractive for nano fabrication [15]. Furthermore, Choudhury et al. found that DLC film consist of gradient layer was yielded finest tribological performances [16]. Wang et al. found that the most adhesive diamond film was the one consist of gradient composite interlayer [17]. The gradient structure has been demonstrated to be effective in enhancing materials properties [18–20]. Inspired by these, our focus is that whether the gradient doping method could combine these contrary properties.

In this present study, the DLC film and N-DLC films with gradient and constant N doping were synthesized by the stable and easily controlled [21] direct-current (DC) magnetron sputtering method.

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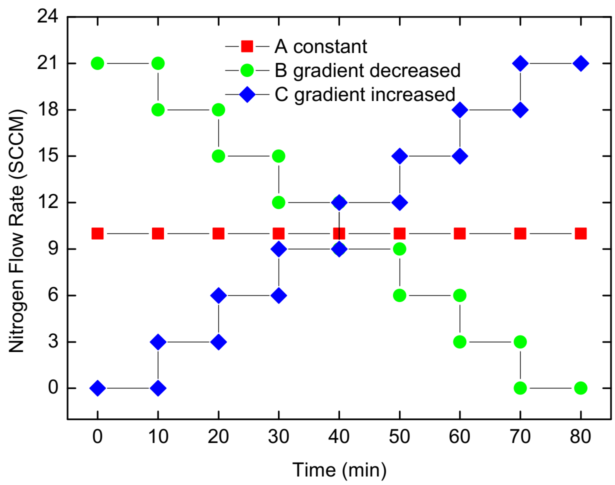

Fig. 1. N flow rate of N-DLC films during deposition. Sample A is the N^C-DLC film, sample B is the gradient decreased doping (N^--DLC) film and sample C is the gradient increased doping (N^+-DLC) film.

Raman spectra, nano-scratch tester, AFM and nano-indenter were used to investigate the effects of gradient N doping on the composition, adhesion, tribological, morphological and mechanical properties of films. The relationship between tribological and mechanical properties was deduced. The relationship between surface roughness and N concentration during the deposition was proposed. The performance of N^G-DLC and N^C-DLC films was evaluated comprehensively.

2. Experimental

The N-DLC films were deposited on silicon (Si) substrates under different dynamic parameters by DC magnetron sputtering method (JGP560-C). The Si (100) substrates (purity ≥ 99.999%) were cleaned with deionized water (PCJ-SF-20), acetone (purity ≥ 99.5%) and ethanol (purity ≥ 99.7%) respectively for 15 min by an ultrasonic cleaner (frequency: 40 KHz ± 10%). The base pressure was 4×10^{-5} Pa which achieved by a turbo-molecular pumping system. The sputtering target was a graphite (purity ≥ 99.999%) wafer with a diameter of 60 mm and a thickness of 3 mm. The sputtering temperature of all films was the same as room temperature (~20 °C). The atmosphere consisted of argon (purity ≥ 99.999%) and N (purity ≥ 99.999%) during deposition. The different N doping concentration was controlled by different N flow rate. The argon flow rate was controlled to be a constant of 35.2 sccm (sccm denotes cubic centimeter per minute at STP). The N flow rate was decreased and increased by gradient in order to obtain N^G-DLC films. The total sputtering time was 80 min per film and the N flow rate was presented in Fig. 1. The N concentration of sample A was controlled to be a constant of 10 sccm. The N concentration of sample B was gradient decreased from 21 sccm to 0 sccm in steps of 3 sccm, while the N concentration of sample C increased from 0 sccm gradient to 21 sccm in steps size of 3 sccm. The pressure was constantly 0.4 Pa and the N-DLC films were synthesized at a set DC power of 160 W and the actual power was 145 ± 1 W.

After deposition, the composition of films was investigated by Raman spectra. The Raman measurements were performed with a Renishawinvia Reflex Raman spectrometer at 514 nm in backscattering geometry, which resulted in an incident power at the sample of approximate 1.7 mW and the spectral resolution obtained was approximate 1–2 cm^{-1}. The adhesion and tribological properties were investigated by a nano-scratch tester (Switzerland, CSM instruments).

All of the scratch tests were performed on the nano-scratch tester. The tester is powered by electromagnetic actuation to achieve unparalleled dynamic range in force and displacement. Prior to and following the scratch test, a single-line-scan of the surface topography is completed for comparing the original surface to the deformation caused by the scratch test. Each scratch test consists of three steps: a single-line pre-scan of the area to be scratched, the ramp-load scratch test, and a final scan to evaluate the residual deformation. In a ramp-load scratch test, a tip is brought into contact with the sample; then, the tip is loaded at a constant loading rate shown in Fig. 2(a), while simultaneously translating the sample. The mechanical properties were investigated by a nano-indenter (Switzerland, CSM instruments) with an increasing load which is shown in Fig. 2(b). The surface morphology and deposition rate were investigated by AFM (Seiko, SPI3800N instrument).

3. Results and discussion

3.1. Composition

As shown in Fig. 3, two Raman peaks near 1580 cm^{-1} (G peak) and 1350 cm^{-1} (D peak) were observed, indicating typical DLC structure characteristics in samples [22,23]. The G peak is caused by the band stretching of all pairs of sp^2 atoms in both rings and chains. The D peak is caused by the breathing modes of sp^2 atoms in rings [24–27].

The three-stage model [28,29] was used for samples because it can be extended to explain the trend of the Raman parameters in any carbon nitride measured at any excitation wavelength [30]. The sp^3 content was calculated by the equation [31]:

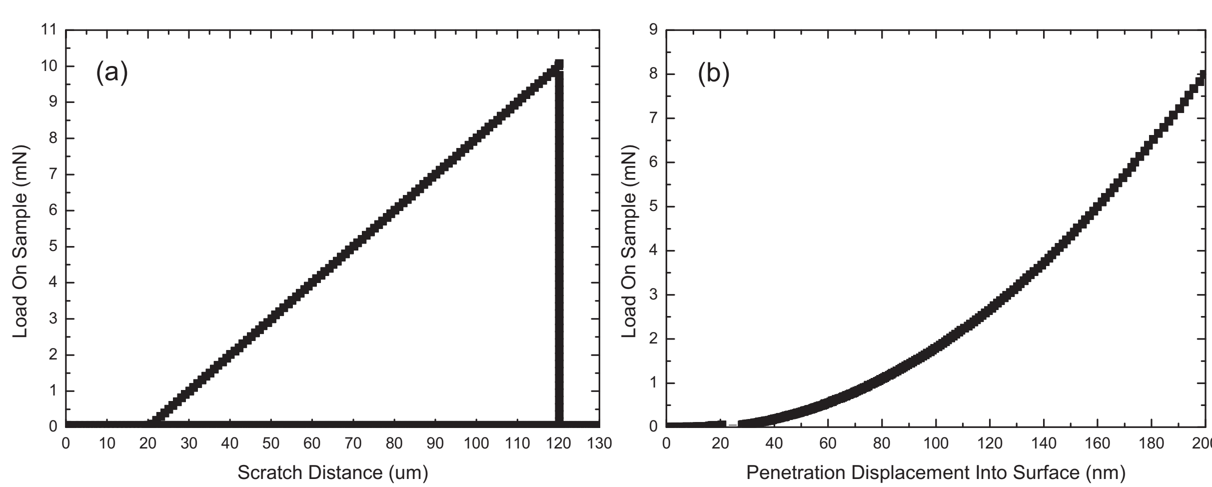

Fig. 2. (a) Load on samples during scratch experiments. The tip was loaded at a constant loading rate while simultaneously translating the sample. (b) Load on samples during indention experiments.