Tribological Properties of Annealed Diamond-like Carbon Film Synthesized by RF PECVD Method

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Diamond-like carbon (DLC) films were prepared on silicon substrates by the RF PECVD (Plasma Enhanced Chemical Vapor Deposition) method using methane (CH_4) and hydrogen (H_2) gas. We examined the effects of the post annealing temperature on the tribological properties of the DLC films using friction force microscopy (FFM). The films were annealed at various temperatures ranging from 300 to 900 °C in steps of 200 °C using RTA equipment in nitrogen ambient. The thickness of the film was observed by scanning electron microscopy (SEM) and surface profile analysis. The surface morphology and surface energy of the films were examined using atomic force microscopy and contact angle measurement, respectively. The hardness of the DLC film was measured as a function of the post annealing temperature using a nano-indenter. The tribological characteristics were investigated by atomic force microscopy in FFM mode.

Keywords : Atomic force microscopy, Diamond-like carbon, Friction force microscopy, Surface roughness, Tribology

1. INTRODUCTION

Due to their high hardness, high electrical resistivity, low IR absorption, transparency to visible light and good chemical inertness, diamond-like carbon (DLC) films have found several important applications in field emission displays[1], solid state devices[2], micro electro mechanical systems (MEMS)[3], and many wear resistant coatings[4]. Some of these applications need stable conditions during their operation against local annealing or addition, etc. However, DLC films suffer from high residual stress and thermal degradation at higher temperatures[5,6].

Various physical and chemical methods, such as sputtering[7], pulsed laser deposition[8], plasma-enhanced chemical vapor deposition[9], and filtered vacuum arc[10] have been employed to synthesize the DLC films. Among these methods, the RF PECVD method has been widely used for the synthesis of DLC thin films, because it uses the standard plasma processing technology that allows for the simple and relatively inexpensive low-temperature coating of a range of temperature sensitive substrates, as well as allowing the film to be uniformly coated on substrates of different shapes and sizes[11] and the DLC properties to be easily controlled by controlling the hydrogen contents in the film[12].

In this work, we used the RF PECVD method to prepare DLC thin films with methane (CH_4) and hydrogen (H_2) gas. The synthesized DLC films were annealed at various temperatures ranging from 300 to 900 °C in steps of 200 °C using RTA equipment in nitrogen ambient. We measured and compared the properties of the post annealed DLC films with structural and tribological methods as a function of the annealing temperature and characterized the friction coefficient of the annealed DLC film with a FFM method.

2. EXPERIMENT

The DLC films were deposited on p-type (100) silicon substrates using the 13.56 MHz RF PECVD method. The substrates were cleaned using the usual RCA method followed by 10 minutes of in-situ H_2 plasma pre-treatment at a gas pressure of 133 Pa (1 Torr) and an RF power of 150 W, in order to remove any contaminants present on the surface and to activate the surface. Methane and nitrogen gases were then introduced into the reaction chamber to grow the films at room temperature. The substrate was heated solely by the plasma during the growth of the film and the deposition time was fixed at 5 minutes 30 seconds for

Table 1. Deposition conditions.

Substrates	p-type Si (100)
Pre-treatment gas	H_2: 80 sccm
Deposition gas	CH_4: 20 sccm H_2: 80 sccm
Working pressure	1 Torr
RF power	150 W
Electrode to substrate distance	7 cm
Deposition time	5 mins 30 secs
Substrate temperature	Room Temperature

every sample. Following its deposition, the DLC film was post annealed with rapid thermal annealing (RTA) equipment in nitrogen ambient. The DLC films were annealed at various annealing temperatures ranging from 300 to 900 °C in steps of 200 °C. The films were maintained at the annealing temperature for 1 min and the rising and falling time were both 30 sec. The experimental parameters used in this study are shown in Table 1.

The thickness and surface morphology of the DLC thin films were analyzed using a surface profiler (Tencor, Alpha-Step 500) and an atomic force microscope (Seiko, SPA-400), respectively. A Raman spectrometer (Jasco, MRS-3000) was used to characterize the structure of the DLC films and a nano-indenter (MTS, Nano-indenter II) was employed to measure their hardness. FFM was used to obtain the friction coefficient from the friction force signals.

3. RESULTS AND DISCUSSION

The Raman spectra (excitation wavelength 532.01 nm and laser power 3.5 mW) of the DLC thin films are shown in Fig. 1(a) as a function of the annealing temperature. Raman data are widely used for the characterization of the structure of DLC films because of their ability to distinguish the sp^3 from the sp^2 bonding type[13]. The Raman spectra in the present study were deconvoluted into two Gaussian peaks which are summarized in Fig. 1(b). The I_D/I_G ratio and G peak position increased as the annealing temperature increased. Such an increase in the I_D/I_G ratio corresponds to an increase and enlargement of the sp^2 clusters in the DLC films[14]. The G peak position in the Raman spectra is related to the sp^2/sp^3 ratio[15]. The G peak position shifted to a higher wavenumber with increasing annealing temperature which corresponds to an increase in the sp^2 bonding fraction[16]. Therefore, the Raman spectrum shows that thermal annealing transforms the DLC structure into a graphite structure[17]. The Raman analysis results indicate that the higher annealing temperature leads to the loss of hydrogen contents in the DLC films and to a transition from sp^3 to sp^2 carbon hybridization, resulting in an increase of the sp^2 clusters in the film.

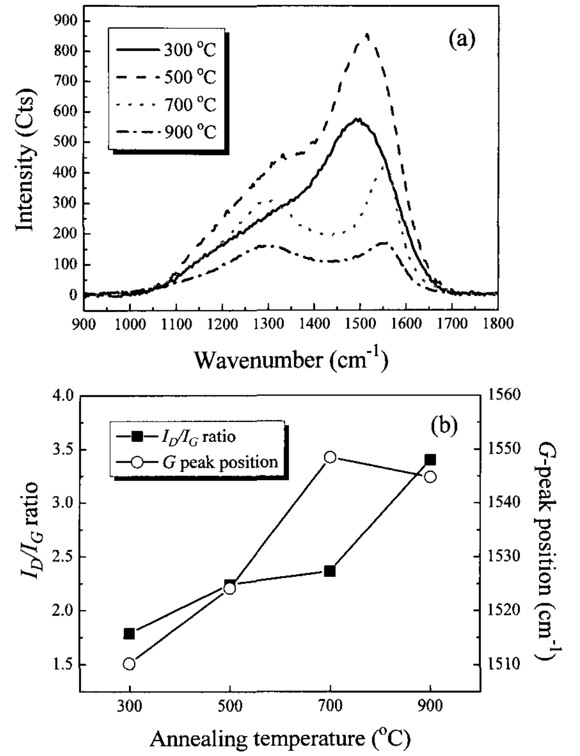

Fig. 1. Raman spectrum of DLC films, (a) Raman spectra as a function of annealing temperature, (b) I_D/I_G ratio and G peak positions as a function of annealing temperature.

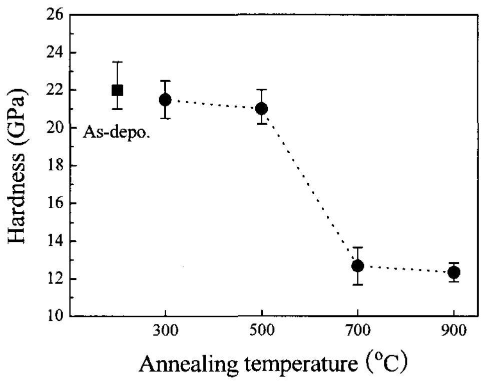

Fig. 2. Hardness of the annealed DLC films as a function of the annealing temperature.

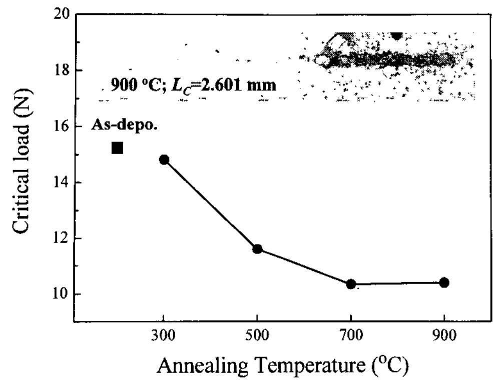

Fig. 3. Critical load of the annealed DLC films as a function of the annealing temperature.

Figure 2 shows the hardnesses of the as-deposited DLC film and the films annealed at 300, 500, 700, and 900 °C obtained from the nano-indenter measurement. The hardness abruptly decreases from 20.3 to 12.7 GPa between 500 and 700 °C. This result is quite consistent with the Raman analysis. The post annealing treatment results in an increase in the graphitic fraction in the film and the clustering of the sp^2 bonded carbon[18].

Figure 3 shows the scratch test result of the annealed DLC film as a function of the annealing temperature, and the upper image is the scratch trace obtained after testing the DLC film annealed at 900 °C. We obtained the critical load of each sample from equation (1).

$$\text{Critical load (N)} = \frac{L_C}{L_T} \times F \quad (1)$$

where the total scratch length (L_T) is 5 mm, the maximum load (F) is 20 N, and the critical scratch length (L_C) is the value obtained from the scratch test measurement.

From this figure, the measured critical scratch length is 2.601 mm for the DLC film annealed at 900 °C, and the critical load of this film obtained from equation (1) is 10.4 N. The length of the scratch trace increases with increasing annealing temperature and the critical load of the annealed films decreases from 14.8 N to 10.4 N as the annealing temperature is increased from 300 to 900 °C. This result indicates that the adhesion strength of the annealed DLC films deteriorated as the post annealing temperature increased[19].

We obtained the friction characteristics using atomic force microscopy (AFM) in FFM mode. The applied force was increased from 4 to 24 nN in steps of 4 nN. Firstly, we obtained the FFM signal during the Fig. 4(a) shows the FFM signals for the as-deposited DLC film. Then, we calculated the friction force (F_t) from equation (2) with the FFM value corresponding to each impressed force[20].

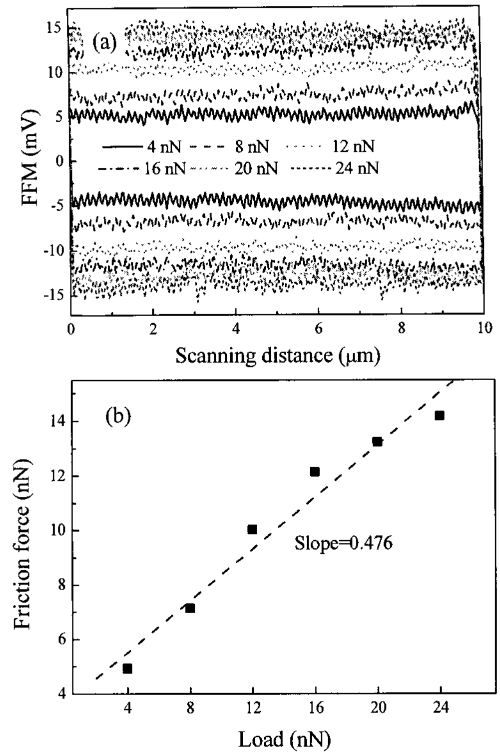

Fig. 4. Friction force microscopy, (a) friction signal of as-deposited DLC film, (b) friction force of as-deposited DLC film.

$$F_t = \frac{0.4 \times (\frac{d}{L}) \times C_t \times FFM(mV)}{S_{dif}} \quad (2)$$

where the cantilever tip length (d) is 2.8 μm, the cantilever arm length (L) is 100 μm, the spring constant (C_t) is 483.3 N/m, the bending sensitivity (S_{dif}) is 40 mV/nm and FFM is the value obtained from the AFM measurement.

Figure 4(b) shows the friction force and fitting line of the as-deposited DLC film. In this figure, the slope of the fitting line corresponds to the friction coefficient of the DLC film.

Figure 5 shows the friction force data with respect to the annealing temperature and their fitting line. We obtained the slopes of each data and the results are summarized in Fig. 6 along with the fitting line. As the annealing temperature increases, the friction coefficient also increases. This result indicates the increase in the size or number of sp^2 domains and graphite crystallites in the annealed DLC film. Moreover, the friction coefficient increases with increasing annealing temperature, which is consistent with the other results in this study.

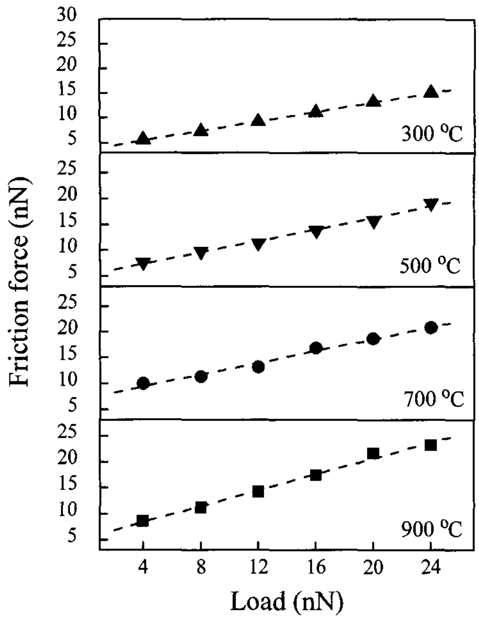

Fig. 5. Friction force of the annealed DLC film as a function of the annealing temperature.

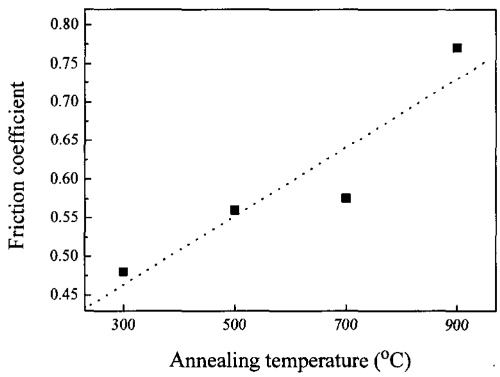

Fig. 6. Friction coefficient of the annealed DLC film as a function of the annealing temperature.

4. CONCLUSION

We investigated the effect of the post annealing of DLC films prepared using PECVD on their tribological properties. The structural properties of the annealed DLC films were characterized by Raman spectroscopy. The I_D/I_G ratios and G peak positions increased with increasing post annealing temperature. The results of the nano-indenter measurements show that the hardness of the annealed DLC films decreases with increasing annealing temperature. The scratch test shows that the annealed DLC films have a large scratch trace and small critical load at higher annealing temperatures. The FFM measurement results show that the friction coefficient increases with increasing annealing temperature. From the above measurements, we conclude that the annealing of the DLC film at higher temperatures results in an increase in the size and density of the sp^2 clusters, resulting in a reduction in the hardness and also the critical load increases friction coefficients.

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