THE INFLUENCE OF REHEAT-TREATMENT ON PROPERTIES OF DIAMOND-LIKE CARBON FILM

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ABSTRACT

Silicon-oxygen and silicon-nitrogen incorporated into diamond-like carbon (DLC) films fabricated from C_2H_2:TMS:O_2 and C_2H_2:TMS:N_2 mixtures were used to study the influence of reheat-treatment on properties of films prepared by plasma-based ion implantation (PBII) technique. The films were heated at 150°C and re-heated at 300°C, 450°C and 600°C, respectively. The structure of the films was analyzed by Raman spectroscopy. Tribological property of the film was performed by ball on disk friction testing. The results indicate that with the increasing reheating temperature, G peak position and friction coefficient increases. Si-O-DLC film shows a friction coefficient of 0.05 before reheating and 0.07 after reheating at 450°C, which is considerable improvement in the tribological property. For Si-N-DLC film, the result shows a friction coefficient of 0.06 before reheating and 0.08 after reheating at 450°C.

1. INTRODUCTION

Diamond-Like Carbon (DLC) film are amorphous film that exhibit properties of high hardness and elastic modulus, low friction coefficients, good wear resistance and excellent corrosion resistance. Therefore, the films are commonly applied in magnetic storage, automobile, tooling, biomedical, and other applications (Kwak, et al., 2005), (Cruz, et al., 2006). Methods for preparing DLC films include ion beam-assisted deposition, magnetron sputtering deposition, plasma assisted chemical vapor deposition and plasma-based ion implantation. However, DLC films have several known limitations. Depending on the environment, the films can have a poor friction coefficient and limited endurance, and low adhesion between the film and substrate due to high intrinsic compressive stress. Moreover, it has been reported that DLC films maintain stable properties up to approximately 400°C, the graphitization process of the samples start at this temperature (Dillon, et al., 1984). This is due to DLC films have low thermal stability at higher working temperatures. Silicon incorporation into DLC films has been proven to overcome some of the stated drawbacks, including low intrinsic compressive stress, good adhesion, and mechanical resistance (Damasceno, et al., 2000). Silicon-oxide-containing DLC film and silicon-nitrogen-containing DLC film presents interesting mechanical, tribological and thermal stability. In early study (Moolsradoo, et al., 2011), the structure of DLC film with silicon and oxygen incorporation (>25 at.%Si, ≤1 at.%O) were affected by the thermal annealing in air at 400°C. The properties of DLC film with silicon and nitrogen incorporation (23 at.%Si, 8 at.%O) was affected by the thermal annealing in air at 500°C (Jongwannasiri, et al., 2013). Currently, there is no report on the deposition of DLC films aimed to study the influence of reheat-treatment on their properties.

In this paper, Plasma based ion implantation (PBII) technique was utilized to prepare silicon-oxygen and silicon-nitrogen incorporation into DLC films. The aim was to study the influence of reheat-treatment on the properties of DLC films.

2. EXPERIMENT

2.1 Experimental Apparatus

A schematic of the PBII apparatus used for the deposition of silicon-oxygen and silicon-nitrogen into DLC films is shown in Fig. 1 (Moolsradoo, et al., 2010). The plasma was generated by a radio frequency (RF, 13.6 MHz) glow discharge and a negative voltage pulse power supply is connected to the sample holder.

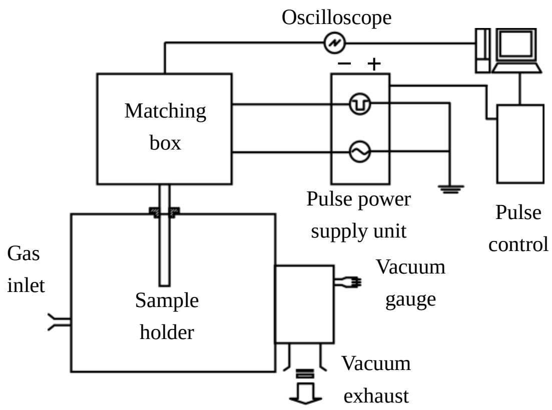

Fig. 1 Schematic of PBII (Moolsradoo, et al., 2010).

2.2 Experimental details

Silicon (100) wafers with 0.7 mm thickness were used as substrates. The wafers were sputter cleaned with Ar^+ for 20 min to remove surface contaminants and surface oxides using a negative bias voltage of -10 kV. The first layer was deposited with CH_4 for 60 min to improve the adhesion between the film and the substrate using a negative bias voltage of -20 kV. The Si-O-DLC and Si-N-DLC films were deposited from gaseous mixture showed in Table 1. The bias voltage was set to -5 kV, at an RF power of 300 W. The pulse frequency was set to 1 kHz at a pulse width of 5 µs and a pulse delay of 25 µs. The deposition pressure was set to 2 Pa. The total deposited thickness of all films was approximately 500 nm. For comparison, pure DLC film was also deposited on Si wafer substrate using C_2H_2 gas by the same deposition process at 2 Pa deposition pressure.

Table 1 Deposition conditions for all films.

Film types	Gaseous Mixture	Flow rate ratio
Si-O-DLC	C_2H_2:TMS:O_2	14:1:2
Si-N-DLC	C_2H_2:TMS:N_2	14:1:2
Pure DLC	C_2H_2	-

* TMS = Tetramethylsilane ($C_4H_{12}Si$)

The DLC, Si-O-DLC and Si-N-DLC films were used to investigate at four levels of reheat-treatment temperature (150°C, 300°C, 450°C and 600°C). All films were first heated (held at temperature) at 150°C for 1 hour and slowly cooled down inside the furnace (the furnace is turned off and the films are let cool down inside). Then, the same samples were re-heated at 300°C, 450°C, and 600°C respectively, with the same re-heat process.

The structure of all films was analyzed using the Raman spectroscopy (JASCO NRS-1000 DT, beam diameter = 4 µm, and wave length = 532 nm). The tribological property of all films was measured using a ball-on disk friction tester (CSEM; Tribometer). A dry sliding test was carried out using a ball indenter, AISI440C (SUS440C) with diameter of 6 mm. The normal applied load was set at 3 N, with a rotation radius of 4 mm, linear speed of 31.4 mm/s, and 6,000 rotations. The tests were performed under ambient air at room temperature with 30-35% humidity.

3. ANALYSIS

3.1 Structure of all films

The Raman spectra obtained are shown in Fig. 2-4. The position of G peak is related to bond-angle disorder or sp^3 bonding content. It is one of important factors governing the quality of the DLC films. Generally, as the G peak decreases, the properties of DLC films approach the properties of diamond.

The pure DLC film shows a broad spectrum composed of a D band (1350 cm^{-1}) and G band (1580 cm^{-1}) which is similar to the peaks observed in conventional DLC film until reheating at 300°C, and the film was completely destroyed at 450°C. Si-O-DLC and Si-N-DLC show broad spectra until reheating at 450°C, and completely destroyed at 600°C.

From Fig. 2, G peak of DLC film shifts from 1509 cm^{-1} (before reheat) to 1524 cm^{-1} with reheating temperature at 300°C. From Fig. 3, G peak of Si-O-DLC film shifts from 1497 cm^{-1} (before reheat) to 1509 cm^{-1} and 1540 cm^{-1} with reheating temperature at 300°C and 450°C, respectively. From Fig. 4, G peak of Si-N-DLC film shifts from 1504 cm^{-1} (before reheat) to 1511 cm^{-1} and 1531 cm^{-1} with reheating temperature at 300°C and 450°C, respectively. Therefore, G peak position of all films shifts towards higher with reheating temperature. These results indicate an increase of number or size of graphitic domains, lead to a loss of film hardness and wear resistance (Moolsradoo, et al., 2011).

In view of the above, the structure of the pure DLC was not affected by the thermal reheating at 300°C, while Si-O-DLC and Si-N-DLC films were not affected by the thermal reheating at 450°C.

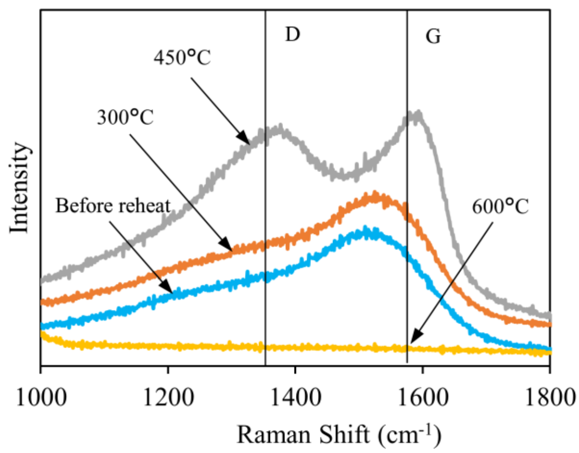

Fig. 2 Raman spectra of pure DLC film.

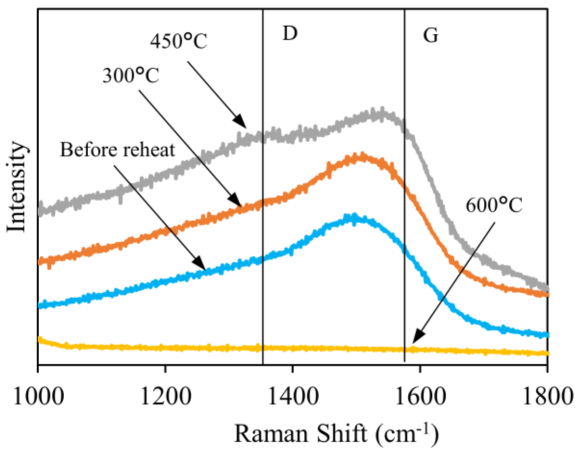

Fig. 3 Raman spectra of Si-O-DLC film.

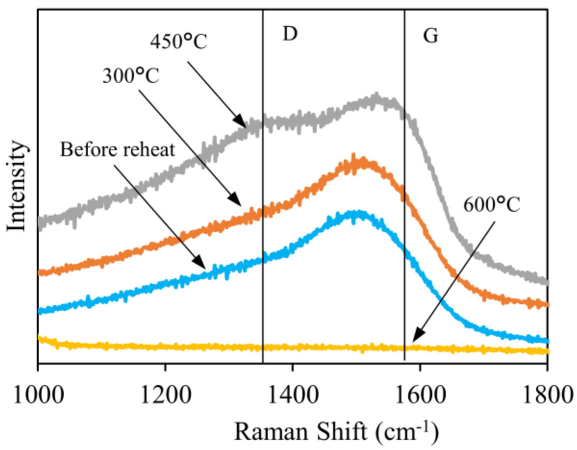

Fig. 4 Raman spectra of Si-N-DLC film.

3.2 Friction coefficient of all films

The friction coefficients of all films measured under ambient air are shown in Fig. 5-7. From Fig. 5, the results of pure DLC film before reheating and after reheating at 300°C were shown to be relatively stable, with friction coefficient of 0.12 and 0.13, respectively. The pure DLC film after reheating at 450°C had an unstable friction coefficient and failed during test. This is due to the graphitization of film structure, as conclude from Raman spectra.

From Fig. 6, the results of Si-O-DLC film before reheating and after reheating at 300°C and 450°C were shown to be relatively stable, with friction coefficient of 0.05, 0.06 and 0.07, respectively.

From Fig. 7, the results of Si-N-DLC film before reheating and after reheating at 300°C and 450°C were shown to be relatively stable, with friction coefficient of 0.06, 0.07 and 0.08, respectively.

The friction coefficients of all films increased with increasing reheating temperature. It is speculated that the film hardness decreases with increasing graphitization, as conclude from Raman spectra. In earlier study (Yang, et al., 2003), it was shown that the DLC films started to be graphitized, which results in softening of the annealed film surface. Moreover, Si-O-DLC film had a lower friction coefficient than Si-N-DLC and pure DLC films. This low friction coefficient is related to the formation of silicon-rich oxide debris and the transferred layer of the silicon oxide on the steel ball surface (Yang, et al., 2002).

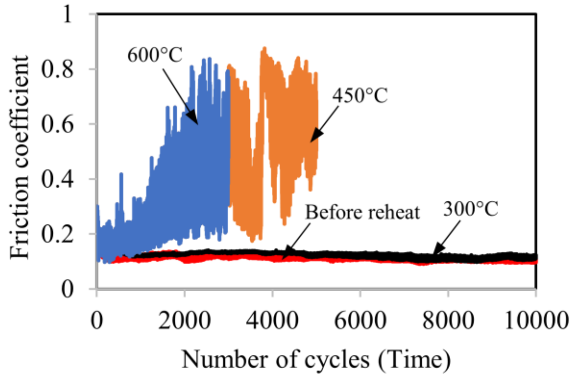

Fig. 5 Friction coefficient of pure DLC film.

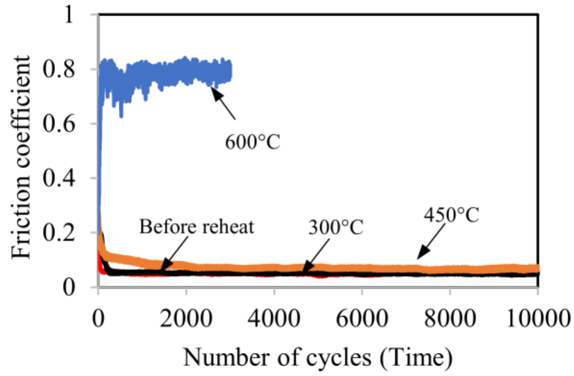

Fig. 6 Friction coefficient of pure Si-O-DLC film.

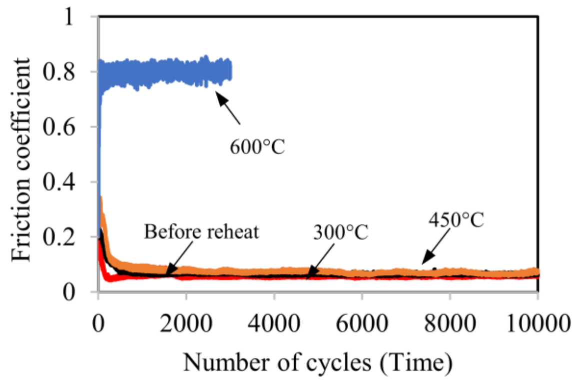

Fig. 7 Friction coefficient of pure Si-N-DLC film.

CONCLUSION

Silicon-oxygen and silicon-nitrogen incorporated into diamond-like carbon films were prepared on Si (100) wafer by the PBII technique. The films heated at 150°C and re-heated at 300°C, 450°C and 600°C, respectively, were investigated in term of their structures and tribological property by using Raman spectroscopy and ball on disk friction testing. It was observed that by increasing the reheating temperature, G peak position of all films towards higher. The structure of the pure DLC film was not affected by the thermal reheating at 300°C, while Si-O-DLC and Si-N-DLC films were not affected by the thermal reheating at 450°C. Si-O-DLC film before reheating and after reheating at 450°C was shown to be relatively stable, with friction coefficient of 0.05 and 0.07. Si-N-DLC film before reheating and after reheating at 450°C was shown to be relatively stable with friction coefficient of 0.06 and 0.08. The friction coefficients of all films increased with increasing reheating temperature. It is speculated that the film hardness decreases with increasing graphitization, as conclude from Raman spectra.

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