

The Effect of Hydrogen on the Tribological Properties of Hydrogenated Amorphous Carbon Films

Jong-Han Shin and Dae-Soon Lim

Dept. of Materials Engineering, Korea Univ., Seoul, Korea
(Received November 5, 1996)

Hydrogenated amorphous carbon films were deposited on silicon substrates by using an RF PECVD. The hydrogen/methane ratio was varied from 50% to 88% to study the effect of hydrogen in the film on the tribological properties. The friction and wear behaviors of the deposited films were investigated by ball-on-disk type wear tester. FT-IR spectra were used to characterize the structure of the films. Tribological properties of carbon films were correlated with their structure such as ratio of "polymer-like" stretching type and that of sp^2 bonding. The result showed that the annealing caused a decrease in the amount of wear of contacted Si_3N_4 balls and a increase in the coefficient of friction. Possible explanation for annealing effect was discussed by the hydrogen desorption.

Key words : Amorphous hydrogenated carbon films, PECVD, Wear, Coefficient of friction, FT-IR, Hydrogen Film structure

I. Introduction

Diamond-like carbon (DLC) film has received increasing attention owing to their unique properties such as high hardness, chemical stability, high thermal conductivity and optical transparency.^{1,3)} Optical coatings, abrasion resisting coatings and electrical devices are potential field of applications.⁴⁾ Since DLC films exhibit low friction with other contacting materials even in the unlubricated conditions, there is growing interest in expanding the applications of DLC films to tribological parts such as the head or drum of a video cassette recorder, hard disk and ball bearings.^{5,7)}

The structure of hydrogenated carbon films can be described as a random network of covalently bonded carbon in hybridized tetragonal and trigonal local coordination, with some of the bonds terminated by hydrogen.⁸⁾ The effect of hydrogen contained in the surface of hydrogenated films on their tribological properties has been discussed by several workers.^{3,9-11)} However, most of hydrogen effects on tribological studies were limited to specific studies such as hydrogen desorption during heating and bonding mixture of carbon hybridization.

In this study, tribological tests were performed on various kinds of carbon films deposited with different hydrogen gas mixture. The "polymer-like", "diamond-like", tetragonal and trigonal bonding ratio were measured by Fourier transform infrared (FT-IR) spectroscopy. An attempt was made to find a structural factor which most probably could affect the tribological behavior of hydrogenated films.

II. Experimental Procedures

1. Deposition of hydrogenated carbon films and

heat treatments

Amorphous hydrogenated carbon films were deposited by a radio-frequency plasma enhanced Chemical Vapor Deposition (RFPECVD) technique. A schematic diagram of the deposition equipment is shown in Fig. 1. A 13.7 MHz radio frequency generator was used to create plasma state. Power of RF generator could be controlled up to 300 watt. Initial vacuum was maintained by mechanical pump. Methane and hydrogen with more than 99.99% purity were delivered to produce a hydrogenated carbon films and flow rate of each gas was independently controlled by mass flow controller (MFC). The substrate temperature during the plasma deposition was lower than about 120°C. The volume ratios of hydrogen were varied from 50 to 88%. Different deposition time was selected for deposition in the different gas ratio to obtain similar film thickness. Film thickness was measured by α -step profilometer. Detailed deposition parameters were tabulated in Table 1.

(100) p-type silicon wafer was used as substrate. Each wafer was lapped and polished according to semiconductor industry standards and fractured into 10×20 mm rectangular plates. These substrates were cleaned with trichloroethylene, acetone and ethyl alcohol for 5 minutes prior to deposition. After cleaning, they were dried and etched for 10 minutes with hydrogen gas in the hydrogen plasma assisted reaction chamber.

2. Annealing and characterization

The film samples were also thermally annealed using rapid thermal annealing (RTA) technique at 300, 400 and 500°C for 30 second. Heating rate by halogen lamp and cooling rate were 10°C/sec and 5°C/sec, respectively.

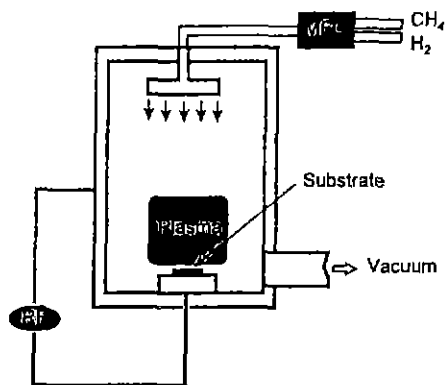


Fig. 1. Schematic diagram of RF plasma-enhanced CVD apparatus.

Table 1. Deposition Conditions of Hydrogenated Amorphous Carbon Films

Sample	Methane flow rate (sccm)	Hydrogen flow rate (sccm)	RF power (W)	Temperature (°C)	Deposition time (sec)	Thickness (µm)
1:1	20	20	200	100-120	2700	1.70
1:2	20	40			3200	1.63
1:3	20	60			3700	1.55
1:4.5	20	90			4200	1.79
1:7.5	20	150			5500	1.95

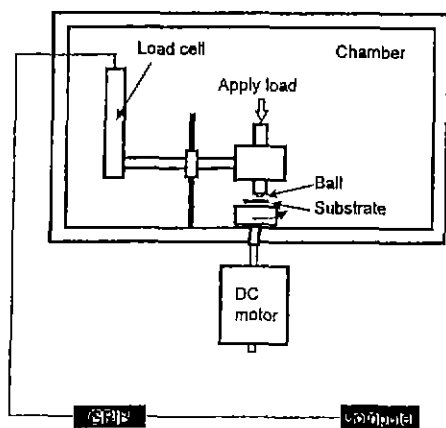


Fig. 2. Schematic diagram of ball-on-disk tribotester.

The structure of the films was characterized by FT-IR spectroscopy. Absorption spectra were obtained from as-deposited and annealed films. Worn surface of the films were also observed by a scanning electron microscope.

3. Tribological tests

The friction and wear tests were performed on a ball-on disk tribometer. A schematic diagram of the tester is shown in Fig. 2. Wear tests were conducted in air at a room temperature. Specimen holder was rotated unidirectionally at a speed of 1600 rpm by DC motor. Silicon nitride ball (6.35 mm in diameter) was loaded by a

dead weight. The frictional force transferred to a load cell was recorded throughout the tests. The wear tests were performed at a normal load of 1.76 and 7.35 N, and sliding speed of 0.4 m/sec. Sliding time for each test was 3600 seconds.

III. Results and Discussion

1. Effect of hydrogen content on the tribological properties of carbon film

Sliding of carbon film against silicon nitride ball produced the wear scar in the ball and the wear track in the film. Measuring the width of the wear track in the film was not easy to detect due to lower wear rate of carbon films. The diameter of wear scar of silicon nitride was measured to compare the relative tribological properties of various kinds of deposited carbon films. The relative wear and coefficient of friction plotted against the hydrogen concentration are shown in Fig. 3. As shown in Fig. 3, the relative wear of silicon nitride varied with hydrogen concentration in the reaction gas. Lowest wear, was observed in carbon film deposited at 75% hydrogen concentration. A trend of inverse relation between wear amount and coefficient of friction should be noted.

In order to better understand the effect of structures of carbon films on observed tribological data, we measured the FT-IR spectra to obtain information about bonding ratio of sp³ to sp².

Typical FT-IR spectrum for carbon films grown is shown in Fig. 4. It can be deconvoluted into 7 different peaks in the region of 2800 to 3100 cm⁻¹ wave number by computer fitting. The absorption bands for hydrogenated carbon are identified and listed in Table 2. The sp³/sp² ratio and "diamond-like"/"polymer-like" bonding ratio¹²⁾ of the films depending on hydrogen concentration are shown in Fig. 5. The friction data show a correlation with "diamond-like"/"polymer-like" bonding ratio and sp³/sp² bonding ratio. The reaction for a minimum values

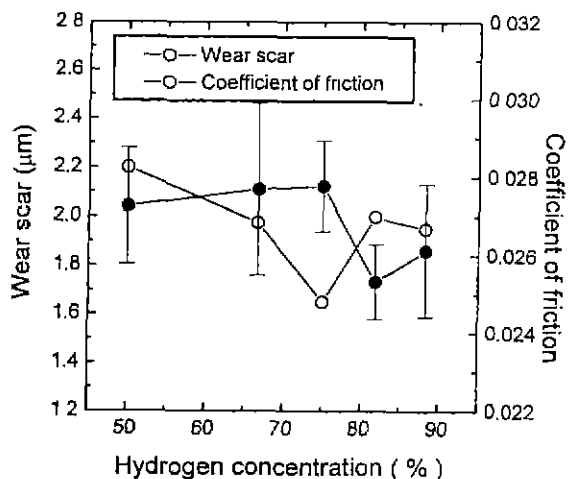


Fig. 3. Wear scar and coefficient of friction of asdeposited hydrogenated carbon films tested at 1.76 N normal load.

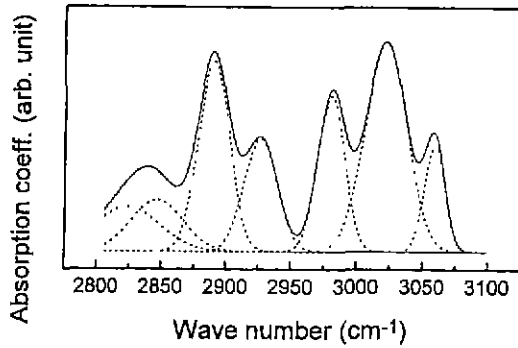


Fig. 4. FTIR absorption spectra of hydrogenated carbon films deposited at 1:2 methane/hydrogen ratio.

Table 2. Predicted FT-IR Absorption Peak Position and Assigned Configurations

Peak position (cm ⁻¹)	Absorption center
2820	N, O related
2850	sym. Sp ³ CH ₂
2890	sp ³ CH
2925	asym. Sp ³ CH ₂
2980	sym. Sp ² CH ₂
3025	sp ² CH ₂
3080	sym. Sp ² CH ₂

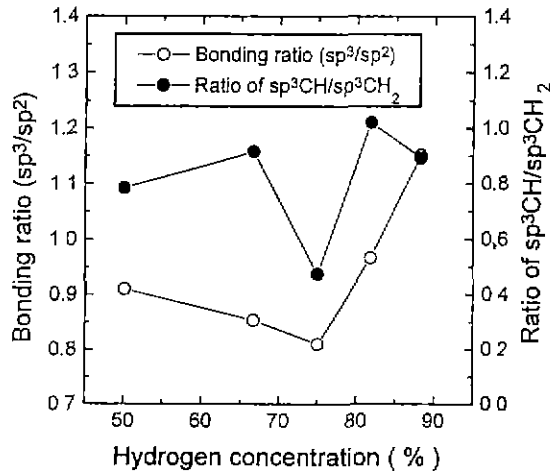


Fig. 5. The sp^3/sp^2 bonding ratio and sp^3CH/sp^3CH_2 ratio at different samples as a function of hydrogen concentration.

near a 75% hydrogen concentration is not clear to explain. The results suggested that tribological properties were strongly influenced by film structures. Fig. 3 and Fig. 5 indicate that increasing ratio of "polymer-like" bonding and sp^2 bonding contributed to lower wear amount of silicon nitride ball.

The typical SEM micrographs of wear tracks of films deposited at two different hydrogen concentrations are shown in Fig. 6. Wear debris generated during sliding

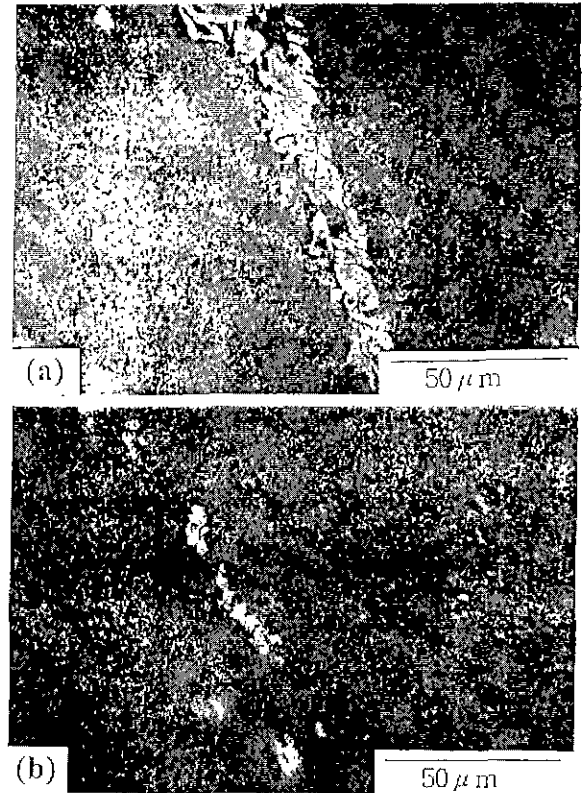


Fig. 6. Scanning electron micrographs of hydrogenated carbon films after tribotest at 1.76 N, deposited at (a) 75% hydrogen ratio, and (b) 82% hydrogen ratio.

and a very smooth surface were observed. The greater amount of wear debris was generated in films containing greater ratio of "polymer-like" bonding and sp^2 bonding. The increasing ratio of "polymer-like" bonding and sp^2 bonding might contribute to lower bonding strength of the film. The film having lower bonding strength was expected to produce greater wear debris against silicon nitride ball. The lower amount of wear of silicon nitride ball might be attributed to less abrasive action of relatively soft carbon film.

2. Effect of thermal annealing of films on tribological properties

Fig. 7 and Fig. 8 show the effect of hydrogen concentration on wear scar and coefficient of friction, respectively. The amounts of wear decreased and the coefficient of friction increased by annealing. Ratio of sp^3CH/sp^3CH_2 bonding and ratio of sp^3/sp^2 after annealing are also shown in Fig. 9 and Fig. 10. Figures indicate that ratio of sp^3/sp^2 were better correlated with the change of wear scar and coefficient of friction.

According to Miyoshi and co-workers, annealing causes hydrogen loss from the surface of the hydrogenated carbon films and the formation of a graphite-like layer.¹³⁾ Fig. 10 shows the portion of sp^2 increased with annealing temperature. As shown in Fig. 8, the coefficient of friction increased by annealing.

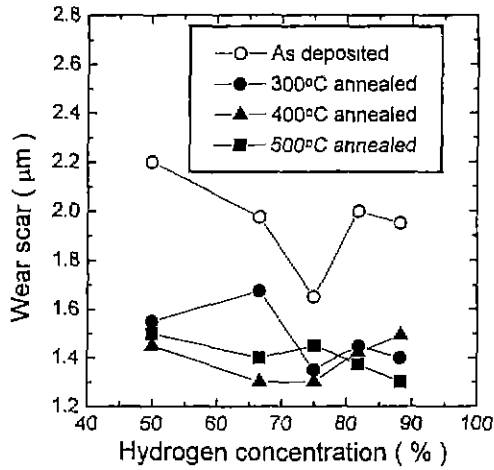


Fig. 7. Wear scar of as-deposited and annealed hydrogenated carbon films at 1.76 N normal load.

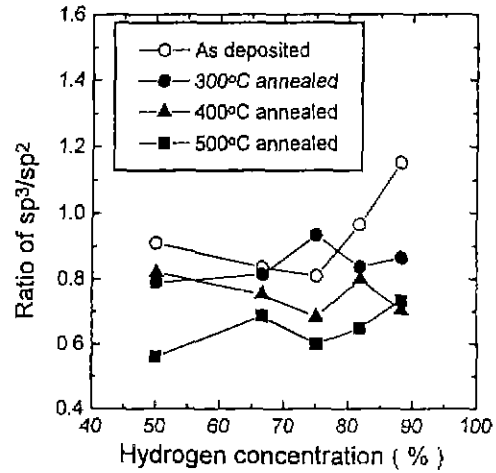


Fig. 10. The sp^3/sp^2 ratio of as deposited and annealed hydrogenated carbon films as a function of hydrogen contents.

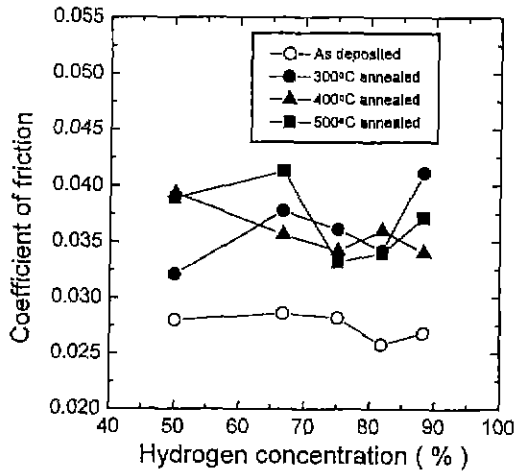


Fig. 8. Coefficient of friction of as-deposited and annealed hydrogenated carbon films at 1.76 N normal load.

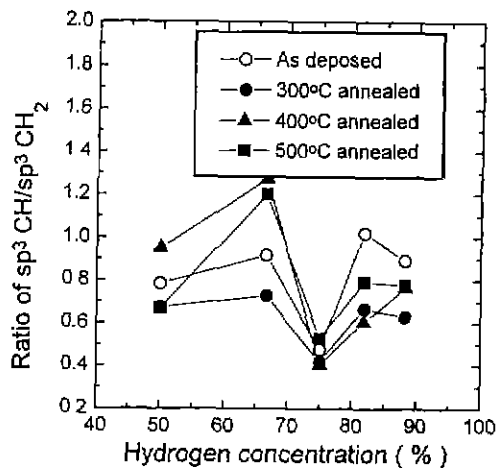


Fig. 9. The $sp^3 CH/sp^3 CH_2$ ratio of as deposited and annealed hydrogenated carbon films as a function of hydrogen contents.

The increasing tendency could not be explained by increasing sp^2 bonding. Hydrogen desorption might be another

factor to explain.¹⁴ When hydrogen is lost from hydrogenated carbon films by annealing, the dangling bonds created cause strong interactions between the contacting surfaces, which increase the coefficient of friction.^{15,16} Weissmantal *et al.* found that the coefficient of friction of DLC films was increased by heating. They also pointed out that an increase of the coefficient of friction was attributed by a loss of hydrogen rather than graphitization of the DLC films.⁶ This study also indicated that the presence of hydrogen in these films was essential for maintaining a low coefficient of friction during wear test.

IV. Conclusions

Hydrogenated carbon films were deposited on silicon substrates by using an RF PECVD apparatus: The effects of hydrogen concentration and annealing on wear and coefficient of friction were studied. The following results were obtained.

1. Tribological properties of silicon nitride ball against hydrogenated carbon film appeared to be strongly dependent upon the structure of individual films. Maximum ratio of "polymer-like" bonding and sp^2 bonding in the film contributed to minimum wear in silicon nitride ball
2. Annealing the deposited films caused a hydrogen desorption and a change in the sp^3/sp^2 bonding ratio. The loss of hydrogen through annealing influenced the increase in the coefficient of friction. The wear of silicon nitride ball were influenced by the sp^3/sp^2 bonding ratio rather than C-H stretching type.

References

1. P. Hedenqvist, M. Olsson and S. Hogmark, *Wear*, **153**, 65 (1992).
2. R. Wei and P. J. Wilber, *Wear*, **162**, 558 (1993).
3. K. Enke, H. Dimigen and H. Hubsch, *Appl. Phys. Lett.*

- 36**[4], 291 (1980).
4. A. Grill, *Wear*, **168**, 143 (1993).
 5. J. F. Braza and T. S. Sudarshan, *Material Sci. and Technol.*, **8**, 574 (1992).
 6. H. C. Tsai and D. B. Bogy, *J. Vac. Sci. Technol.*, **A6**[4], 3287 (1987).
 7. S. Agarwal and E. Li, *IEEE Trans. On Mage.* **29**[1], 264 (1993).
 8. B. Dischler, A. Bubenzer and P. Koidl, *Solid State Commun.*, **48**, 105 (1983).
 9. S. Miyake, *Surf. Coat. Technol.*, **54-55**, 563 (1992).
 10. V. V. Khvostov, M. B. Guseva, V. G. Babaev and O. Yu. Rylova, *Solid State Commun.*, **55**[5], 443 (1985).
 11. K. Enke, *Thin Solid Films*, **80**, 227 (1981).
 12. Z. Liu, R. Zhang, M. Liu, G. Yang, Q. Liu, R. Wang, W. Wang, W. Ji, X. Ji and D. R. He, *J. Materials Science*, **28**, 5313 (1993).
 13. K. Miyoshi, *Surf. Coat. Technol.*, **44**, 799 (1990).
 14. R. Memming, H. J. Tolle and P. E. Wierenga, *Thin Solid Films*, **143**, 31 (1986).
 15. L. P. Hayward, *Surf. Coat. Technol.*, **49**, 554 (1991).
 16. H. Zaidi, A. Hezin, M. Nivoit and J. Lepage, *Appl. Surf. Sci.*, **40**, 103 (1989).