ELSEVIER

Materials Science and Engineering A 483–484 (2008) 245–247

MATERIALS SCIENCE & ENGINEERING A

www.elsevier.com/locate/msea

Investigation of fracture characteristics in thermally aged thin films of diamond-like carbon

Seung Baek [a], Se-June Parks [b], Kwang-Real Lee [b], Chang-Sung Seok [a,*]

[a] *School of Mechanical Engineering, Sungkyunkwan University, 300 Cheoncheon-dong, Jangan-gu, Suwon, Gyeonggi-do 440-746, Republic of Korea*
[b] *Future Technology Research Division, Korea Institute of Science and Technology, Republic of Korea*

Received 6 June 2006; received in revised form 17 October 2006; accepted 17 October 2006

Abstract

To investigate the chemical and mechanical stability of diamond-like carbon films at 300 °C, we thermally aged the films for different aging times (0: virgin, 24, 48 h). From the Raman spectra analyses, the indentation tests, and the total work fracture data, we confirmed that the aged sample-2(precursor gas: C_6H_{14}) had better mechanical characteristics and thermal stabilities than the aged sample-1(precursor gas: C_6H_6). Also, the fracture toughness is found to decrease with increasing ratio of the intensities of the D- and G-peaks in Raman spectroscopy.

Keywords: DLC; Aging; Indentation; Fracture toughness

1. Introduction

Diamond like carbon (DLC) films cannot maintain their good properties at high temperatures (above 300 °C) because of the reduction in the sp^3/sp^2 ratio [1]. In this study, we studied the change of fracture toughness and the ratio of the intensities I(D)/I(G) of two prominent Raman peaks of an aged DLC specimen in air (aging temperature: 300 °C, aging time: 0, 24, 48 h) by using indentation and Raman spectroscopy. The true fracture toughness of the aged DLC specimen, excluding the influence of the substrate, was determined by using the method of Nastasi et al. [2]. Raman spectroscopy was used to characterize the structure of the DLC films.

2. Sample preparation

DLC films(thickness: 1.5 μm) were deposited on p-type (1 0 0) silicon films by using C_6H_6 and C_6H_{14} plasma produced with a 13.6 MHz RF source. In RF-plasma-assisted chemical vapor deposition, the films were deposited at a negative bias voltage of 400 V at a deposition pressure of 10 mbar. The DLC samples were heated in a furnace in air at 300 °C, exposing them to heat for 24 or 48 h. After each exposure, the DLC samples were allowed to cool to room temperature.

3. Raman spectroscopy and indentation

Raman spectroscopy has been performed on virgin and aged samples. Raman spectra were obtained by using an argon ion laser operating at a wavelength of 514.5 nm. Indentation experiments were conducted with a Vickers micro-indenter and a fully calibrated Nano Indenter XP. Indentation fracture tests using various loads (mass of 20, 35, 50, 200, 300, 500 g) were performed on the undoped (1 0 0) silicon wafer and DLC on silicon, respectively. Five measurements were taken for each load. Nastasi et al. [2] suggested a method to determine the fracture toughness of a coated material by using the total work of fracture. They also reported that this method could be used to calculate the true fracture toughness of DLC on a silicon system, excluding the influence of the substrate on the fracture toughness.

$$K_t = \sqrt{\left(G_s + \frac{2d}{\pi c}(G_f - G_s)\right)\left(E_s + \frac{2d}{\pi c}(E_f - E_s)\right)}, K_f = \sqrt{G_f E_f}, \left[\left(\frac{C_0}{C}\right)^3 - 1\right] = \frac{2d}{\pi C}(G_f - G_s) \quad (1)$$

where, d is the film thickness, C is half the radial crack length in the coated substrate and C_0 is half the crack length in the

* Corresponding author. Tel.: +82 31 290 7446; fax: +82 31 290 7482.
E-mail address: seok@skku.edu (C.S. Seok).

0921-5093/$ – see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.msea.2006.10.178

uncoated substrate at the same indenter load. E_s is the modulus of the substrate, and E_f is the modulus of the film. G_f and G_s are the critical energy-release-rates in the film and the substrate.

4. Experiment results and discussion

4.1. Raman spectra analysis and material property

The information about the structure of aged DLC films was obtained by using Raman spectroscopy. Spectra were measured in the range from 500 to 2000 cm^{-1}. For quantitative analysis, the Raman spectra of all samples were fitted to two Gaussian peaks denoted as the D-peak and the G-peak. Generally, G-band means graphite structure located at approximately 1530–1580 cm^{-1}.

As shown in Table 1, with increasing aging time, the D-peak and the G-peak move to a higher wave-number. For the virgin specimen of sample-1, the D-peak was located at 1344.3 cm^{-1} and the G-peak at 1530.1 cm^{-1}. With increasing aging time, the G-peak of sample-1 moved to a higher wave-number from 1530 to 1581.2 cm^{-1} and the intensity ratio I(D)/I(G) increased from 0.31 to 0.87. These phenomena reflect strong graphitization of the DLC films due to the breakup of the sp^3 structure at high temperatures. As discussed above, the peak position shift and the I(D)/I(G) of sample-1 specimens dramatically changed, but those of sample-2(hexane) specimens did not. By comparing the Raman spectra and material properties of the aged samples, we confirmed that aged sample-2 have better thermal stability than aged sample-1. As shown in Fig. 1, the atomic weight of oxygen slightly decreased and film thickness of sample-1 increased from 1.5 to 1.52 μm with increase of aging time.

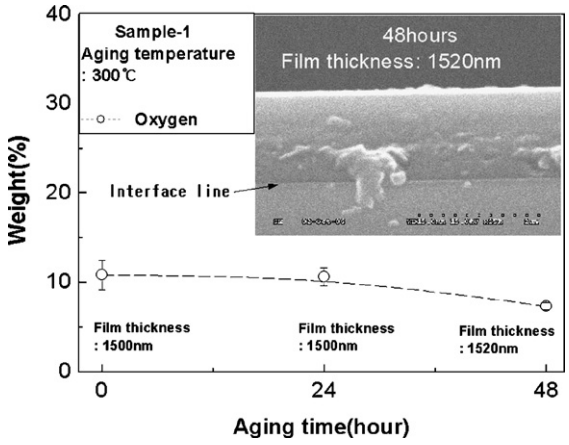

Fig. 1. Weight (%) of oxygen vs. aging time for sample-1.

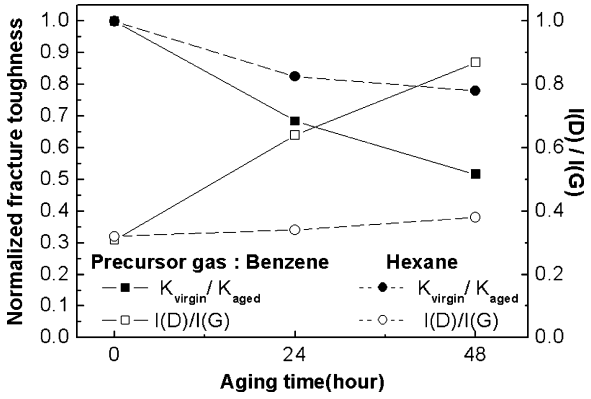

Fig. 2. Normalized fracture toughness vs. I(D)/I(G) for samples.

4.2. Fracture toughness vs I(D)/I(G)

Fracture toughness tests were performed by using a nano-indenter XP (using a Vickers indenter) and a Vickers micro-indenter with loads ranging from 20 to 500 g.

True fracture toughness of the aged DLC specimen, excluding the influence of the substrate, was determined by using Nastasi et al. method. The indentation fracture toughness of the aged sample-1 and sample-2 films excluding the influence of the substrate were 7.7, 14.8 $MPam^{0.5}$, respectively. Fig. 2 shows the change of the normalized fracture toughness ratio ($K_{virgin\ film}/K_{aged\ film}$) and intensity ratio $I(D)/I(G)$ of the samples by thermal aging, respectively. The values of the material properties of sample-1 decreased much more than those of sample-2, as shown in Table 1. This result was in good agreement with those of the Raman spectra analysis. These results revealed that sample-2 films had better mechanical characteristics and thermal stabilities than sample-1 films. Fig. 2 shows the fracture toughness of the aged DLC films with aging time as a function of the intensity ratio I(D)/I(G). From these figures, we confirmed that the decrease of the fracture toughness associated with the graphitization of the DLC films after aging was due to the damage of the

Table 1
Material properties of samples and substrate with aging conditions

Sample	Aging temperature/aging time	D-peak (cm^{-1})	G-peak (cm^{-1})	I(D)/I(G)	Young's modulus (GPa)	Hardness (GPa)
	25 °C/Virgin	1344.3	1530.1	0.31	112.7	16.3
Sample-1 (Benzene)	300 °C/24 h	1368.4	1579.8	0.64	86.2	6.3
	300 °C/48 h	1404.8	1581.2	0.87	71.9	2.8
	25 °C/Virgin	1344.6	1537.4	0.32	182.7	26.0
Sample-2 (Hexane)	300 °C/24 h	1361.0	1550.2	0.34	175.9	26.4
	300 °C/48 h	1361.7	1551.2	0.38	177.4	27.0
	25 °C/virgin	–	–	–	185.9	13.71
Silicon (1 0 0)	300 °C/24 h	–	–	–	181.5	13.77
	300 °C/48 h	–	–	–	182.5	13.66

original structure. Therefore, the decrease in fracture toughness with the increase of I(D)/I(G) ratio demonstrated the dependence of the intensity ratio I(D)/I(G) on the fracture toughness of aged DLC films.

5. Summary

To investigate the chemical and mechanical stability of DLC films at 300 °C, DLC films were deposited on p-type (1 0 0) silicon films by using C_6H_6 and C_6H_{14} precursor gases. From the Raman spectra analyses, the indentation tests, and the fracture toughness analyses, we confirmed that the aged sample-2 films (precursor gas: C_6H_{14}) had better characteristics, such as mechanical and thermal stability, than the aged sample-1(precursor gas: C_6H_6) films. Also, the fracture toughness is found to decrease with the increase of I(D)/I(G) ratio.

Acknowledgement

This paper was supported by Samsung Research Fund, Sungkyunkwan University, 2005.

References

[1] M.L. McConnell, D.P. Owoling, N. Donnelly, K. Donnelly, Surf. Coat. Technol. 116–119 (1999) 1133.
[2] M. Nastasi, P. Kodali, K.C. Walter, J.D. Embury, J. Mater. Res. 14 (1999) 2173–2180.