

Characteristics of bonding structures of diamond-like carbon films deposited by radio frequency plasma-enhanced chemical vapor deposition

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Diamond-like carbon (DLC) films were deposited on p-type (100) Si wafers using a plasma-enhanced chemical vapor deposition system and their structural bonding characteristics and mechanical properties were investigated as a function of the mixture ratio of methane-hydrogen gas and the bias voltage. It was found that the deposition rate increased with an increase in the flow rate of methane in the gas mixture and an increase in bias voltage. The sp^3/sp^2 ratio of carbon in the films and the hardness of the films increased with an increase in the flow rate of hydrogen in the gas mixture and an increase in the bias voltage.

Key words: Diamond-like carbon, PECVD, Bonding structure, Hardness.

Introduction

Diamond-like carbon (DLC) films synthesized by the plasma decomposition of hydrocarbon gas have been considered for many industrial applications because DLC films are easier to produce than diamond films while still exhibiting excellent physical and chemical properties close to those of diamond; high hardness, high optical transparency in the visible and infrared regions, high electrical resistivity and good chemical stability [1-3]. In particular, DLC films have been extensively studied for wear resistant coatings because of their low wear coefficient [4-6].

DLC films have been prepared by a number of deposition methods [7-9]. Thus, for example, the radio frequency plasma-enhanced chemical vapor deposition (RF-PECVD) method can fabricate DLC films at a high deposition rate over a large area [10]. The mechanical properties of DLC films deposited by this method depend strongly on deposition processing parameters, such as total gas pressure, bias voltage and gas flow rate [11].

Unfortunately, the wide spread use of DLC films has been limited by poor adhesion of these films to substrates, because of large compressive stresses induced in the films during the deposition process. It has been reported that the residual stresses in these DLC films arise from a change in the local chemical bonding and changes in bonding angle and bonding length, caused by the ions penetrating into the film surface during processing [12, 13]. Therefore, the hydrogen content of

the DLC films and the characteristics of the bonding structure are important parameters in the control of physical properties [14, 15].

When using a hydrocarbon gas as a starting material in the RF-PECVD process, plasma chemical species which contain hydrogen are generated, and so it is usual for hydrogen to be deposited into the films simply because hydrogen can bond to carbon in the films during film growth. This trapped hydrogen also helps to determine the local bonding structure, such as sp^3 or sp^2 type, produced in the film.

Thus, in general, DLC films have C-C bonds as well as C-H bonds the degree of C-H bonding, which has a relatively low energy, depends on the precise detailed deposition conditions, as these control ion energy [10]. It has also been reported that the hardness of films can be improved by reducing the hydrogen content in the films through control of the flow rate of reaction gases [16].

The aim of this study is to improve the mechanical properties of DLC films by controlling the residual stresses in the DLC films deposited by a RF-PECVD method. In particular, we have paid attention to how the variation of the bonding structure and hydrogen contents in the film depend on the bias voltage and flow rate of reaction gases, and how these in turn relate to the hardness of the films.

Experimental

The RF-PECVD system used consists of a capacitively-coupled, asymmetric plasma reactor driven by a 13.56 MHz rf-power supply. A negative bias voltage was generated at the lower electrode where rf-power was supplied. The source gases were supplied uniformly by

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a shower head distribution system. The pressure in the chamber during deposition processing was controlled precisely with an automatic pressure controller system with a booster pump and throat valve.

P-type (100) silicon wafers were used as substrates for the DLC films. There were cleaned using an ultrasonic cleaner and then dried by nitrogen gas before being loaded into the reactor. Each substrate was placed on the lower electrode then water cooled. Methane (99.99%) and hydrogen (99.99%) gases were used as reaction gases. After a pressure in the reactor of 9.3×10^{-6} Pa was attained by ion pumping, the substrate surface was etched by a hydrogen plasma for 10 minutes in the reactor with a rf power of 80 W prior to DLC film deposition. For the etching process, the flow rate of hydrogen gas was fixed at 50 sccm and the pressure was kept at 11.2 Pa.

After the etching process was complete, the pressure was reduced to 9.3×10^{-6} Pa again before the reaction gases were supplied to the reactor chamber.

For the DLC deposition, the flow rate of methane and hydrogen in the reaction gases were varied from 10 to 30 sccm and from 30 to 50 sccm, respectively, with a total flow rate of the reaction gases fixed at 60 sccm. The working pressure was fixed at 11.2 Pa and the bias voltage was varied from 300 to 500 V. The deposition conditions are summarized in Table 1.

The thickness of the deposited DLC films was measured by cross-sectional observation using a scanning electron microscope (SEM, Jeol, JSM-5900 LV, Japan). Fourier transform infrared spectroscopy (FT-IR, Nicolet, Magna-IR 760 spectrometer, USA) analysis was performed for wave numbers ranging from 500 to 4000 cm^{-1} to characterize the bonding in the films and in particular, the relative ratio of sp^3 to sp^2 C-H bonding in the DLC film. The relative hydrogen content was estimated by integrating the total area of the absorption peaks in the C-H stretching vibration range of 2700 to 3100 cm^{-1} [17].

Raman spectroscopy (Raman, Jobin-Yvon, T64000, France) with an argon ion laser of 35 mW power at a green wave length of 514.5 nm was used to evaluate the material properties of the deposited films in the wavenumber range from 1000~1800 cm^{-1} . The Raman

parameter, peak position and FWHM, and intensity ratio (I_D/I_G) of D and G peaks in the DLC films were estimated from the peak analysis using a Gaussian line shape for the deconvolution of Raman spectra [17]. The hardness of the deposited film was measured using an ultra micro-indentation system equipped with a diamond indenter. (nano-indentor, CSIRO, UMIS-2000). The indentation tests were performed under an applied load of 5mN using a Berkovich-type tip.

Results and discussion

The thickness of the DLC films deposited as a function of bias voltage and the ratio of methane and hydrogen gas is shown in Fig. 1. It is seen that to a fair approximation the film thickness linearly increases with an increase in the bias voltage. This can be attributed to an increase in the number of radicals which participate in the reaction, resulting from enhanced ionization and dissociation of methane gas because of the increased electron energy in the plasma with an increase in the bias voltage [18].

At a constant bias voltage, the film thickness decreases with an increase in the flow rate of hydrogen gas. This is attributed to a decrease in the number of radicals which help to form the film, because of the decrease in the flow rate of methane gas. A further factor for the decrease in the film thickness with an increase in the flow rate of hydrogen gas is thought to be the consumption of CH_3 radicals and hydrogen etching of the films. The CH_3 radicals, which contribute significantly to film deposition, are able to bond to hydrogen ions at the film surface and/or in the plasma and subsequently methane gas and are then drawn away from the film while hydrogen ions not bonded to CH_3 radicals are able to etch the deposited film surface [19].

Relevant aspects of the Raman spectra of the DLC films deposited as a function of bias voltage and ratio of flow rate of methane and hydrogen gas are shown in

Table 1. Typical experimental conditions used for the DLC film deposition process

Substrate	p-type Si(100) wafer
Reaction gas	CH_4 , H_2
Biased negative voltage	-(300~500)V
Base pressure	9.3×10^{-6} Pa
Working pressure	11.2 Pa
Total gas flow rate	60 sccm
CH_4	10~30 sccm
H_2	30~50 sccm
Deposition time	1 hr

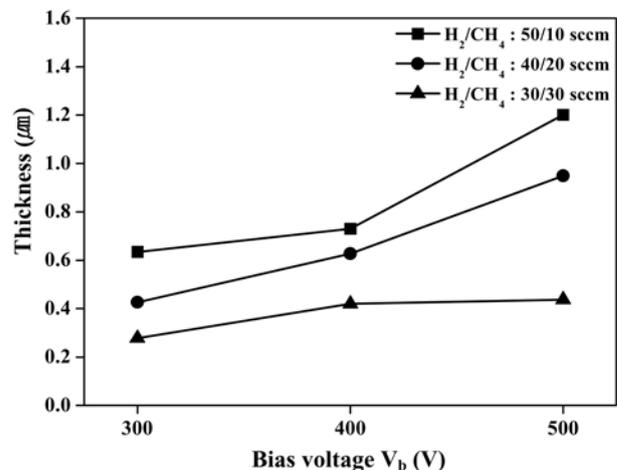


Fig. 1. Thickness of the DLC films as a function of bias voltage for various gas flow rates.

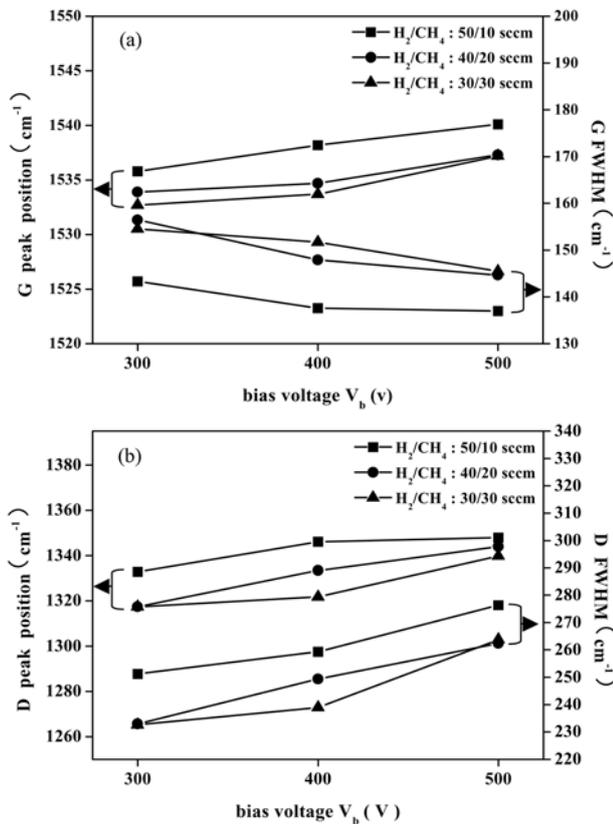


Fig. 2. Peak position of (a) G and (b) D lines respectively as a function of bias voltage for various gas flow rates.

Fig. 2. The peaks of the typical DLC film are seen as a disordered D-peak at about 1350 cm^{-1} and a graphite-like G peak at about 1535 cm^{-1} . These two peaks are due to the sp^2 -bonded carbon phase [20].

As the bias voltage increases, the D and G line positions shift to higher frequencies, the width of the G line decreases and the width of the D line increases. These phenomena can be understood in terms of tighter-bonding angle and bonding length distributions and the formation of a micro-crystalline graphite structure as the bias voltage increases [21].

In addition, the shift and increased width of the D line can be attributed to the decrease of the hydrogen content in the films as the bias voltage increases [22]. The ratios of the integrated intensities of the D and G lines (I_D/I_G) as a function of bias voltage and gas flow rate ratios are shown in Fig. 3.

It is seen from Fig. 3 that the ratio of the I_D/I_G increases with an increase in bias voltage. This is thought to be due to the decrease of hydrogen content in the film and disappearance of disorder in the bonding angle and/or the formation of the micro-crystalline graphite structure [23]. Tsai and Bogy [21] reported that the increase of the I_D/I_G ratio was caused by the increase of the D line intensity and the decrease of the G line intensity, resulting from a decrease of the crystal size in the basal plane of graphite and the disappearance

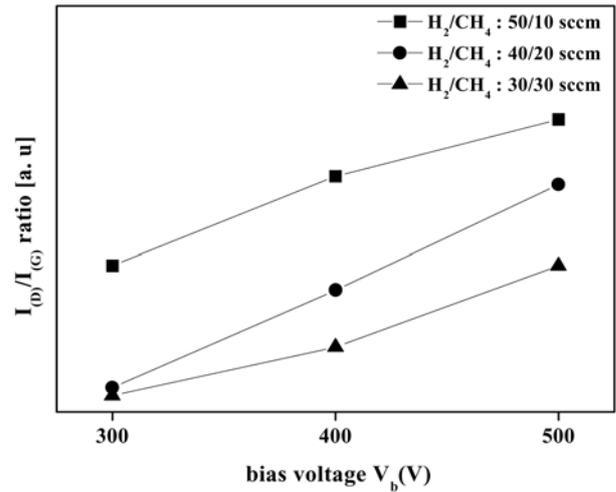


Fig. 3. Ratio of the integrated peak intensities of the D and G lines as a function of bias voltage and gas flow rate ratios.

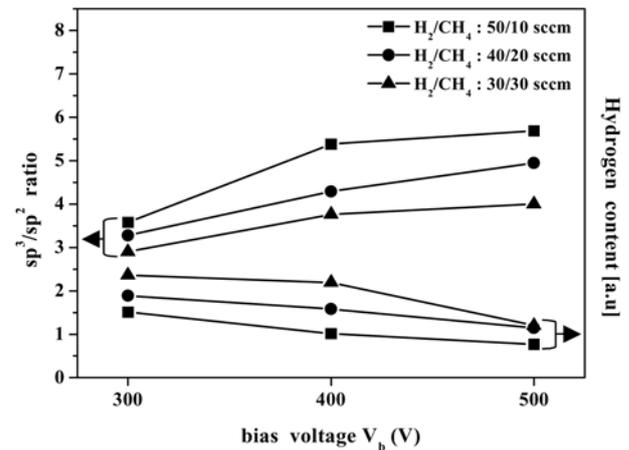


Fig. 4. sp^3/sp^2 ratio and hydrogen content as a function of bias voltage and gas flow rate ratios.

of disorder and decrease of hydrogen content with increasing bias voltage are thought to result in a decrease in the residual stress in the film.

Figure 4 shows the relationship between the relative sp^3/sp^2 ratio and hydrogen content as a function of a bias voltage and gas flow conditions determined by FT-IR. The bonding structure and wavenumber of peaks according to the corresponding C-H stretching of the DLC films are given in Table 2 [17].

Table 2. Distribution of the absorption peaks in the C-H stretching region

Wave number (cm^{-1})	Bond type
2850	sp^3 C-H ₂
2870	sp^3 C-H ₃
2920	sp^3 C-H
2970	sp^3 C-H ₃
3000	sp^2 C-H
3060	sp^2 C-H

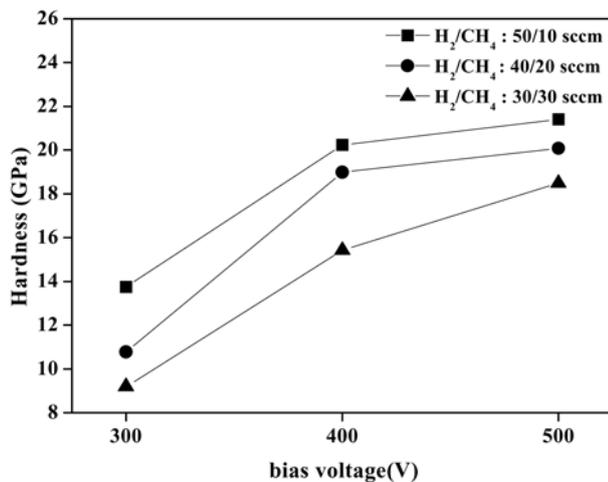


Fig. 5. Typical hardness of deposited the DLC films as a function of bias voltage for various gas flow rates.

The sp^3/sp^2 ratio increases with bias voltage. This is thought to be because the energy of ion bombardment increases with an increase in the bias voltage and therefore these ions penetrate relatively deeply into the growing film surface to form bonds in a bulk region of the film, thereby increasing locally the density of the film. This is because the carbon atoms inside the DLC film prefer to bond with a sp^3 structure than in the sp^2 structure as the density increases [24].

As the flow rate of hydrogen gas in the reaction gas and bias voltage both increase, the ability of the hydrogen atoms to dissociate becomes easier and therefore the amount of hydrogen in the plasma increases, thereby enabling the dissociated hydrogen atoms to etch the carbon in the sp^2 structure. Therefore the ratio of sp^3/sp^2 increases. The reduction of hydrogen content in the film as the bias voltage increases occurs because of the destruction of the relatively weak C-H bonding by collision from highly energetic ions.

In general, as the energy of the deposited ion increases, the bonding structure of the DLC films has a tendency to form relatively stable C-C bonding configurations through the bonding with carbon resulting from the reduction in hydrogen content by ion bombardment from the weak C-H bonding [25, 26]. Grille et al. [13] reported that the content of hydrogen in the films decreases with increasing ion energy because of an increased dissolution of carbonized hydrogen. An increase of the ratio sp^3/sp^2 and a reduction of hydrogen content in the deposited thin films can be both expected to contribute to an increase in the film hardness.

Figure 5. shows the hardness of the DLC films measured by a nano-indentor. It is seen that the hardness of the deposited DLC films increases with an increase in bias voltage and flow rate of hydrogen. These results agree very well with the FTIR results in which the hardness increases with an increase of the ratio sp^3/sp^2 and

reduction of hydrogen content in the films.

Summary

The DLC films were deposited using methane-hydrogen mixed gases by a rf-PECVD system. The film thickness increases as the bias voltage and flow rate of methane increase, and it was confirmed that it is possible to control the bonding structure of the DLC film and the hydrogen content in the DLC film by a control of the bias voltage and flow rate of the reaction gases. As the bias voltage and flow rate of the hydrogen gas in the reaction gases increase, the sp^2 bonding concentration of the deposited films disappeared and the sp^3 bonding concentration increased and therefore the hydrogen content in the films decreased so that the hardness of the films was increased.

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References

1. J.W. Zou, K. Schmidt, K. Reichelt, and B. Dischler, *J. Appl. Phys.* 67 (1990) 487-494.
2. S. Praver, R. Kalish, N. Adel, and V. Richter, *J. Appl. Phys.* 61 (1987) 4492-4500.
3. J. Wagner and P. Lautenschlager, *J. Appl. Phys.* 59 (1986), 2044-2047.
4. H. Kakaue, T. Mitani, H. Kurokawa, Y. Yonezawa and H. Yoshino., *Thin Solid Films* 212 (1992) 240-244.
5. J.C. Angus, and F.J. Jansen, *J. Vac. Sci. Technol. A6* (1988) 1778-1782.
6. V.K. Kudoyarova, A.V. Chernyshov and T.K. Zvonareva, *Surf. Coat. Technol.* 100 (1998) 192-195.
7. Jerome J. Cuomo, James P. Doyle, John Bruley, and Joyce C. Liu, *Appl. Phys. Lett.* 58 (1991) 466-468.
8. F. Davanloo, E.M. Juengerman, D.R. Jander, T.J. Lee, and C. B. Collins, *J. Appl. Phys.* 67 (1990) 2081-2087.
9. P. Reinke, S. Scheiz, W. Jacob, and W. Möller, *J. Vac. Sci. Technol. A10* (1992) 434-438.
10. J.W. Zou, K. Reichelt, K. Schmidt, and B. Dischler, *J. Appl. Phys.* 65 (1989) 3914-3918.
11. K.K. Hirakuri, N. Mutsukura and Y. Machi, *Vacuum* 46 (1995) 57-60.
12. Sung-Jin Cho, Kwang-Ryeol Lee, Kwang-Yong Eun, Jun Hee Hahn and Dae-Hong Ko, *Journal of the Korean Ceramic Society.* 35[8] (1998) 813-818.
13. A. Grill, B.S. Meyerson, V.V. Patel, J. A. Reimer and M. A. Petrich, *J. Appl. Phys.* 61 (1987) 2874-2877.
14. Seong S. Choi, D.W. Kim, J.W. Joe, J.H. Moon, K.C. Park and J. Jang, *Mater. Sci. Eng. B46* (1997) 133-136.
15. Weng-Jin Wu, Min-Hsiung Hon, *Surf. Coat. Technol.* 111 (1999) 134-140.
16. Z. Jiang, C.J. Lu, D.B. Bogy, C.S. Bhatia, T. Miyamoto. *Thin Solid Films.* 258 (1995) 75-81.

17. V. Paishin, E.I. Meletis, S. Ves and S. Logothetidis, *Thin Solid Films* 270 (1995) 165-172.
18. G.J. Vandentop, M. Kawasaki, R.M. Nix, I.G. Brown, M. Salmeron, and G.A. Somorjai., *Phys. Rev. B*41 (1990) 3200-3210.
19. A. Tabata, S. Fujii, Y. Suzuoki, T. Mi-zuami, and M. Ieda, *J. Phys. D*23 (1990) 316-320.
20. T. Sato, S. Furuno, S. Iguchi and M. Hanaboss., *Appl. Phys. A*45 (1988) 355-358.
21. H. Tsai and D.B. Bogy, *J. Vac. Sci. Technol. A*5 (1987) 3287-3312 (1987).
22. L.A. Farrow, B.J. Wilkens, A.S. Gozdz, and D.L. Hart, *Phys. Rev. B*41 (1990) 10132-10137.
23. R.O. Dillon, J.A. Woollam, and V. Katkanant, *Phys. Rev. B*29 (1984) 3482-3489.
24. J. Robertson, *Mater. Sci. Eng. R*37 (2002) 129-281.
25. Sunil Kumar, *Appl. Phys. Lett.* 58 (1991) 1836-1838.
26. S.F. Yoon, K.H. Tan, Rusli, J. Ahn, and Q.F. Huang, *Diam. Relat. Mater.* 9 (2000) 2024-2030.