

Structure and Mechanical Properties of Si Incorporated Diamond-like Carbon Films Prepared by PACVD

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Although tribological behaviors of Si incorporated DLC films have been intensely investigated, their mechanical properties were not consistent among previous publications. The present work reported the structural change by adding Si, and their effects on the mechanical properties. Si incorporated DLC films were deposited using mixtures of benzene and diluted silane with hydrogen of various volume fractions. We could obtain the films of X_{Si} (defined by the Si fraction without considering hydrogen) ranging from 0.001 to 0.21, and found that the mechanical properties of the films changed significantly in the range less than $X_{Si}=0.06$. In this range, the hardness and stress increased with X_{Si} . For higher content of Si, the hardness and stress showed saturated behavior with X_{Si} . This behavior was discussed in terms of the changes in atomic bond structures.

Key words : Diamond-like carbon, Si incorporation, Mechanical properties, Structural change

I. Introduction

Hard diamond-like carbon (DLC) coatings, are expected to act as low friction wear resistant materials. However, it is well known that the test environment such as humidity affects the tribological performance, even if DLC films generally show good chemical inertness.⁽¹⁻³⁾ For an example, the friction coefficient of the coatings in ambient atmosphere is relatively high ranging from 0.1 to 0.4, while in low moisture or in high vacuum the value is as low as 0.02.³⁾ In order to reduce the environmental dependence, various metals such as Fe, Mo or Ti, have been added to the films.^{4,5)} These attempts were partly successful in that the friction coefficient in ambient environment can be reduced to 0.1. However, the lower friction coefficient could not be observed in metal incorporated DLC films. Recently, many investigations have been focused on the tribological behaviors of Si incorporated DLC films, which show very low friction coefficients (<0.1) in various test environments.⁶⁻¹⁰⁾

Although many investigations were focused on the tribological behaviors of Si incorporated DLC films, only a few reports were found on the changes in structure and mechanical properties. In the present work, we report the effect of Si incorporation on the mechanical properties such as hardness, elastic modulus and residual stress that can be intimately related to the tribological behavior. The hardness of DLC films would be proportional to the degree of 3 dimensional inter-links of sp^2 clusters of 1 or 2 nm in size.¹¹⁾ The residual stress can also increase with the inter-links, because the distortion

of atomic bond angles and/or lengths should be proportional to the content of the inter-links in amorphous materials. In contrast to carbon, silicon can have only sp^3 bonds which might increase the 3 dimensional inter-links. Higher hardness and residual stress are thus expected when Si is incorporated to the DLC films. However, some previous investigations reported that the hardness and residual stress were reduced by Si incorporation,¹⁰⁾ which are not consistent with this speculation.

In the present work, content of Si in DLC films was varied in wide range of X_{Si} , defined by the fraction of Si without considering hydrogen, from 0 to 0.21. We found that a small amount of Si ($X_{Si} < 0.06$) could significantly increase the hardness, residual stress and elastic modulus. However, the mechanical properties were not linearly proportional to the content of Si incorporated. A saturated behavior was observed.

II. Experimental

Si incorporated DLC films were deposited on p-type Si (100) wafer by radio frequency plasma assisted chemical vapor deposition (r.f.-PACVD). Substrates were placed on the water cooled cathode to which 13.56 MHz r.f. power was delivered through an impedance matching network. Reaction chamber was evacuated by a turbo molecular pump to 2×10^{-4} Pa. Prior to the deposition, the substrates were sputter cleaned by an Ar plasma for 15 min. The films were then deposited at a bias voltage of -400 V and a pressure 1.33 Pa. Mixtures of benzene and diluted silane with hydrogen ($SiH_4:H_2=10:90$) gases were used

for the deposition. Deposition rates decreased from 85 nm/min to 12 nm/min with increasing the volume fraction of diluted silane gas from 0 to 95%. This decrease would result from increasing hydrogen fraction in the reaction gas. The deposition time was thus adjusted to obtain about 1 μm thick films. The film thickness were measured by an Alpha-step profilometer.

The carbon and silicon concentrations of the films were measured by Rutherford backscattering spectrometry (RBS) using 2.2 MeV $^4\text{He}^{++}$ ion beam at a scattering angle of 170° . By simulation of the spectra using RUMP, we could obtain the Si/C ratio in the films. The hydrogen concentrations were obtained from elastic recoil detection (ERD) spectra. The structures of the films were analyzed by FTIR and Raman spectra. FTIR absorption spectra were obtained in diffuse reflectance Fourier transformation (DRIFT) mode at a resolution of 4 cm^{-1} and averaged over 16 scans. In order to remove the absorption bands originated from the environment, the analysis chamber was purged by dry nitrogen before the analysis. Macro Raman spectra were obtained using Ar ion laser at a resolution 5 cm^{-1} and averaged over 5 scans.

Hardnesses and elastic moduli of the films were measured by a nano-indentor (Nano InstrumentTM II of Nano Instrument Inc.). Normal loads for the measurement were varied from 0.5 to 3 mN. The relative errors in the hardness and elastic modulus which is mainly due to the errors in stiffness estimation were less than 10%. For the residual stress measurement, thin ($210 \pm 10\ \mu\text{m}$ thick) Si strips of size $5\text{ mm} \times 50\text{ mm}$ were also used as the substrates. All the film/substrate composite were convex, showing that the residual stress was compressive. The curvature of the composite was measured by a laser reflection method. The residual stress of the film was then calculated from the equilibrium equation of bending plates.

III. Results and Discussion

Fig. 1 shows the X_{Si} values in the films measured by RBS spectra and surface heights of ERD spectra. In the present experimental condition, the X_{Si} increased from 0 to 0.02 as diluted silane fraction increased from 0 to 60%. Further increasing diluted silane fraction significantly increased the X_{Si} up to 0.21 at the diluted silane fraction of 95%. It was thus possible to investigate the changes in the structure and properties when very small amount of Si was incorporated in the films. The surface heights of the ERD spectra were compared in qualitative manner, because of the uncertainty in scattering cross section of the hydrogen recoil. Quantitative analysis of hydrogen using a standard sample of known hydrogen content is in progress. Hydrogen content in the film slightly decreased, while the hydrogen content in the reaction gas increased. This result agrees with the previous in-

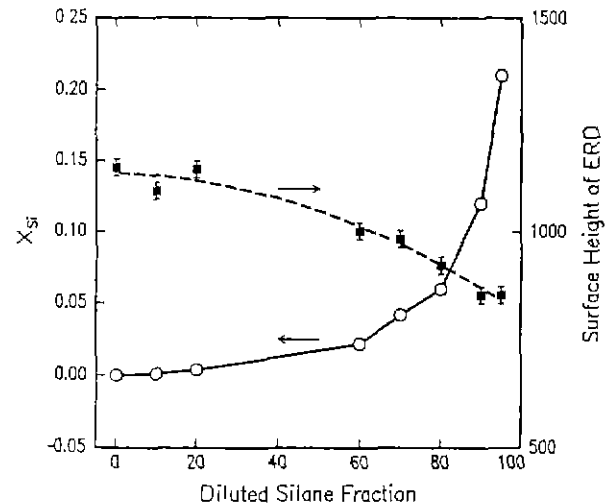


Fig. 1. Composition variation with diluted silane fraction.

vestigations on the effect of hydrogen dilution that the hydrogen content in the film is independent of the hydrogen content in the reaction gas.¹²⁾ This behavior can be understood by considering that the bond strength of C-H (338.3 kJ/mole) is larger than that of Si-H (≤ 299.2 kJ/mole).¹³⁾ It would be more plausible that Si-H bond is broken by ion bombardment during the film growth.

Raman spectra of DLC films can be deconvoluted by two Gaussian peaks which are respectively corresponding to D and G peaks of solid carbon materials as shown in Fig. 2.¹⁴⁾ Fig. 3 shows the dependence of the center of the G-peak on X_{Si} values. Si incorporation in the films resulted in the shift of G-peak center to lower wavenumber. This shift is known to be due to the increase in the fraction of sp^3 bonds in the films.¹⁴⁾ It can be thus said that Si atoms in the film enhanced sp^3 bonds, especially when higher content of Si was in-

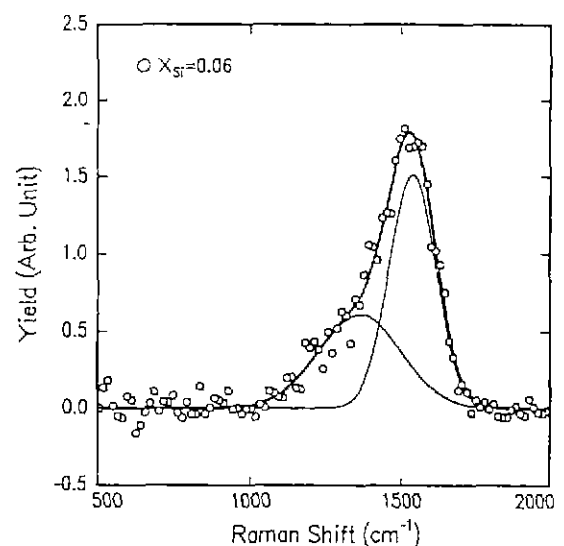


Fig. 2. Typical Raman spectrum of Si incorporated DLC films.

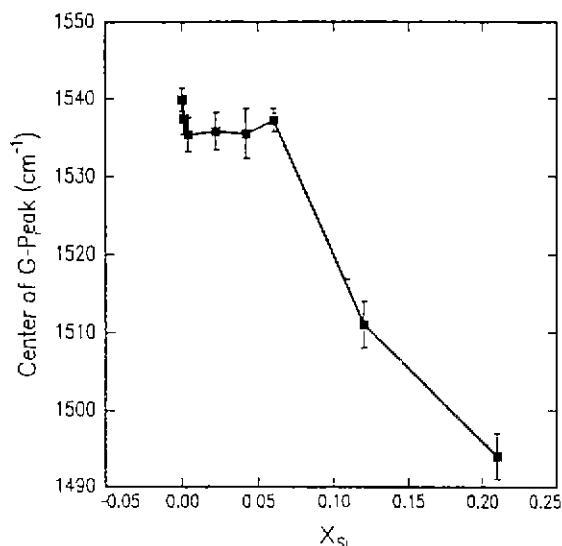


Fig. 3. Shift of G-peak center with increasing X_{Si} .

corporated.

Fig. 4 shows the dependence of the residual stress, hardness and elastic modulus on X_{Si} values. All the mechanical properties showed identical behavior that the values significantly increase when small amount of Si was incorporated. However, these values were saturated or showed a maximum when X_{Si} was larger than 0.06. Comparing with the data in Fig. 1 and Fig. 3, it can be said that neither hydrogen content nor sp^3 bond fraction could explain this behavior of the mechanical properties. The mechanical properties of DLC films will be discussed by the atomic bond structures observed in FTIR spectra

Fig. 5 shows the FTIR spectra of the films. In order to compare the content of each bond in the films, FTIR absorption spectra were normalized by the film thickness. Successive curves were translated upward for the ease of comparison (Numbers on the spectra are the X_{Si} values of the films). Without Si, the spectrum is the typical one for DLC films characterized by a smeared sp^2 and sp^3 bonded C-H stretching absorption band near 3000 cm^{-1} and a small sp^1 bonded C-H stretching absorption band near 3300 cm^{-1} . C-CH₃ bending (1370 and 1450 cm^{-1}) and sp^2 C=C stretching (1600 cm^{-1}) bands are observed in the region of $1000\text{--}2000\text{ cm}^{-1}$.

With increasing Si content, the first observable change in the spectra was disappearance of the sp^1 bonded C-H stretching band. The sp^1 C-H absorption band was not observed when X_{Si} was equal to 0.022. Other changes were hardly observed in the spectra. Since the sp^1 C-H bonds play a role of network termination, this change would increase the 3 dimensional inter-links of sp^2 clusters, which results in the increase of the stress, hardness and elastic modulus as shown in Fig. 4.

When higher content of Si ($> 10\text{ at.}\%$) was incorporated in the films, Si-H stretching band (2100 cm^{-1}) and Si-CH

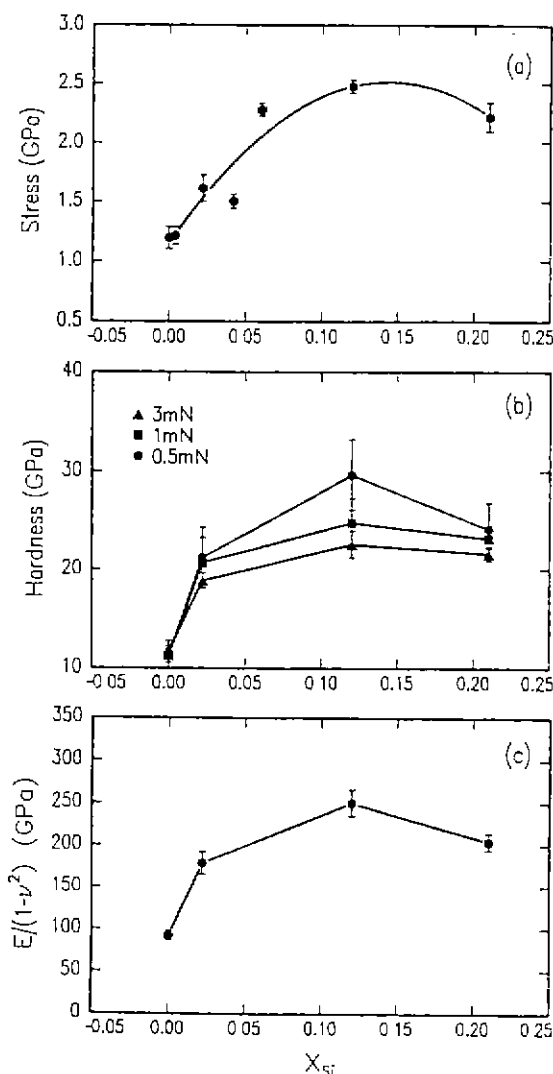


Fig. 4. Dependence of mechanical properties on X_{Si} . (a) Residual stress (b) Hardness (c) Elastic modulus.

stretching and/or bending and wagging band (780 cm^{-1}) became apparent. sp^2 C=C stretching absorption band near 1600 cm^{-1} was also enhanced by Si incorporation. This enhancement would result from symmetry breaking of the aromatic sp^2 clusters by Si substitutes for the carbon atoms in the clusters as in the nitrogen incorporated films.¹⁵ These spectral changes imply that when higher amount Si is incorporated, carbon atoms in sp^2 clusters are substituted by Si atoms being also terminated by hydrogen. When large amount of Si was incorporated, therefore, all the incorporated Si did not increase the 3 dimensional inter-links due to the hydrogen termination. =CH wagging peak near 1000 cm^{-1} was also enhanced by Si addition. Sugimoto et al reported the changes in FTIR spectrum of Si incorporated DLC film during annealing.¹⁶ They showed that the =CH wagging peak was related with the reconstruction of the carbon network by annealing. Hence, it is presumable that short range order was enhanced when large amount of Si was incorporated.

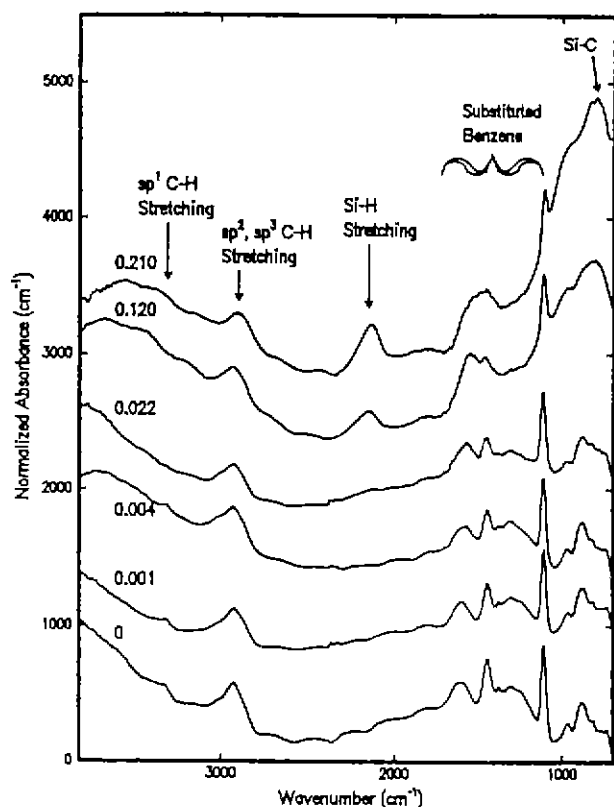


Fig. 5. FTIR spectra of Si incorporated DLC films.

This assumption also agrees with the structural model supposed by Robertson.¹⁷ The saturated behavior of the mechanical properties with Si content seems to result from these changes in the atomic bond structures: hydrogen terminated Si and enhanced short range order in carbon network.

IV. Conclusions

The most significant contribution of the present work is to show that the effect of Si on the mechanical properties of DLC films was dependent on the content of added Si. The first apparent effect of Si incorporation was to reduce the content of sp^1 C-H bond, resulting in significant increase in hardness, residual stress and elastic modulus. When a large amount of Si was incorporated, however, all of the incorporated Si did not play a role to increase the 3 dimensional inter-links. Whereas the incorporated Si substitute the carbon atoms in sp^3 clusters, large fraction of Si was also terminated by hydrogen. It should be also noted that the Si addition enhanced the short range order which would be able to reduce the residual stress of the films by reducing the distortion of bond angle or/and bond length.

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References

1. R. Memming, H. J. Tolle and P. E. Wierenga, "Properties of Polymeric Layers of Hydrogenated Amorphous Carbon Produced by Plasma-activated Chemical Vapour deposition Process," *Thin Solid Films*, **143**, 31-41 (1986).
2. J. Koskinen, "Abrasive Wear Resistance of Ion-deposited Hard Carbon Films as a Function of Deposition Energy," *J. Appl. Phys.*, **63**, 2094-2097 (1988).
3. K. Enke, "Some new Results on the Fabrication of and the Mechanical, Electrical and Optical Properties of I-carbon Layers," *Thin Solid Films*, **80**, 227-234 (1981).
4. E. Bergmann and J. Vogel, "Tribological Properties of Metal/carbon Coatings," *J. Vac. Sci. Technol.*, **A4**, 2867-2869 (1986).
5. C. P. Klages and R. Memming, "Microstructure and Physical Properties of Metal-containing Hydrogenated Carbon Films," *Mater. Sci. Forum*, **52/53**, 609 (1989).
6. H. Dimigen, H. Hubsch and R. Memming, "Tribological and Electrical Properties of Metal-containing Hydrogenated Carbon Films," *Appl. Phys. Lett.*, **50**, 1056-1058 (1987).
7. K. Oguri and T. Arai, "Tribological Properties and Characterization of Diamond-like Carbon Coatings with Silicon Prepared by Plasma-assisted Chemical Vapour Deposition," *Surf. Coat. Technol.*, **47**[1-3], 710-721 (1991).
8. T. Hioki, Y. Itoh, A. Itoh, S. Hibi and J. Kawamoto, "Tribology of Carbonaceous films Formed by Ion-beam-assisted Deposition of Organic Materials," *Surf. Coat. Technol.*, **46**, 233-243 (1991).
9. S. Miyake, T. Miyamoto and R. Kaneko, "Microtribological Improvement of Carbon Film by Silicon Inclusion and Fluorination," *Wear*, **168**[1-2], 155-159 (1993).
10. J. Meneve, R. Jacobs, F. Lostak, L. Eersels, E. Emkempeneer and J. Smeets, "Micromechanical Behaviour of Amorphous Hydrogenated Silicon Carbide Films," *Proc MRS*, **308**, 671-676 (1993).
11. J. Robertson and E. P. O'Reilly, "Electronic and Atomic Structure of Amorphous Carbon," *Phys Rev. B*, **35**, 2946-2957 (1987).
12. K.-R. Lee, unpublished work.
13. CRC Handbook of Chemistry and Physics, 68th ed., CRC Press, Boca Raton (1987).
14. M. Yoshikawa, "Raman Spectra of Diamondlike Amorphous Carbon Films," *Mater. Sci. Forum*, **52/53**, 365-385 (1989).
15. J. H. Kaufman and S. Metin, "Symmetry Breaking in Nitrogen-doped Amorphous Carbon: Infrared Observation of the Raman-active G and D Bands," *Phys. Rev.*, **B39**, 13053-13060 (1989).
16. I. Sugimoto and S. Miyake, "Lubricating Performance Enhancement of Amorphous Silicon Carbide Films by Annealing Effects and Microbeam Analyses of the Tribological Interface," *J. Appl. Phys.*, **66**[2], 596-604 (1989).
17. J. Robertson, "The Electronic and Atomic Structure of Hydrogenated Amorphous Si-C Alloys," *Phil. Mag.*, **B** **66**[5], 615-638 (1992).