MEASUREMENT OF ELASTIC PROPERTIES OF DIAMOND-LIKE CARBON FILMS USING A SIMPLE MICRO-FABRICATION

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1. INTRODUCTION

Amorphous hard carbon films such as diamond-like carbon (DLC) or tetrahedral amorphous carbon (ta-C) have unique combination of physical and chemical properties similar to diamond. The unusual combination of hardness, wear resistance, coefficient of friction, optical transparency and chemical inertness has motivated studies for various applications. High ratio of elastic modulus to mass density of DLC film has also attracted much attention for the applications using high acoustic wave velocity. Among the applications are overcoats for speaker diaphragm and surface acoustic wave devices [1,2]. These applications need accurate measurement of the elastic properties of the thin films.

The elastic modulus of thin films is generally different from that of the bulk materials mainly due to defects or textures in the thin films. Furthermore, the properties of DLC films can be varied in a wide range by changing the deposition condition [3]. It is thus desirable to measure the elastic properties of as deposited DLC films. The elastic modulus of thin films has been measured by various methods, i.e. nanoindentation, Brillouin light scattering, ultrasonic surface wave measurement, bulge test and vibration membrane method. However, these techniques need sophisticated instruments and analysis techniques or delicate micro machining processes.

Typical DLC films have high residual compressive stress up to 10GPa [3]. Although the residual stress is one of the major reasons for poor adhesion, we could use the residual stress to measure the elastic properties. The residual stress of DLC films can be determined from the curvature of the film/substrate composite [4]. If one can measure the strain of the film required to adhere on the substrate, biaxial elastic modulus would be thus obtained from a simple stress-strain relation of elastically isotropic thin films.

In a previous work, we have demonstrated a method to measure the strain of DLC films by simple micro-fabrication process [5]. The method results in unstressed DLC bridges between DLC patches, which enables us to measure the strain of DLC films during the residual stress relaxation. Because the bridges were free from the mechanical constraint of the substrate, the shape of the bridge appeared sine wave of one wavelength that is equal to the bridge length. Since this phenomena is essentially the same as the buckling of the plate, the stain of the bridge can be derived by the classical buckling theory [5]. Biaxial elastic modulus was thus obtained from the strain and the residual stress that can be independently measured from the curvature of film/substrate composite. The validity of the present method was tested in the present work by comparing the results with those obtained by the nanoindentation and sonic vibration method.

2. EXPERIMENTAL

13.56MHz r.f. glow discharge of C_6H_6 was employed for the DLC film deposition. Details of the deposition equipment were described elsewhere [6]. The deposition pressure was fixed at 1.33Pa. However, the negative self bias voltage was varied from 100 to 550V by adjusting the supplied r.f. power. We deposited the DLC films on SiO_2 sacrificial layer of thickness 0.5μm which was grown on Si (100) wafer by thermal oxidation. The DLC films were patterned by a conventional lithography to obtain thin DLC bridges between 100μmX327μm DLC patches. Photoresist was spin coated on the DLC films and developed using a mask pattern. Fig. 1 shows the schematic of the mask pattern. In order to investigate the effects of bridge length and width, we varied the length from 60 to 150μm and the width from 12 to 15μm. Exposed DLC film was etched by oxygen plasma and the sacrificial SiO_2 layer was then removed by

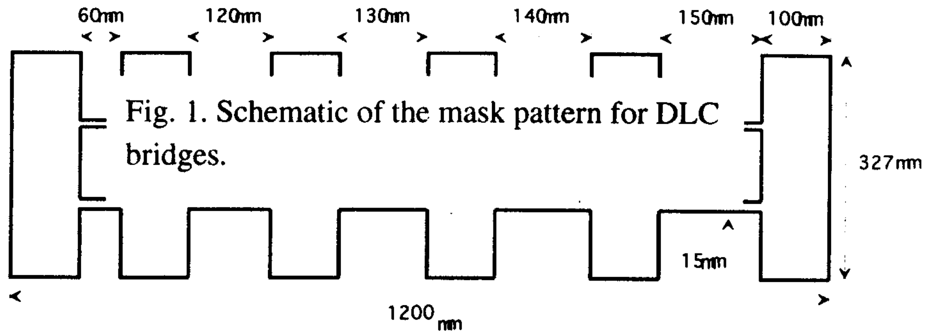

Fig. 1. Schematic of the mask pattern for DLC bridges.

an buffered oxide etcher (BOE). The DLC film was chemically so inert that we could not observe any surface damage or change in the film thickness after the etching process. The etched samples were wet cleaned in sequence using deionized water, ethanol and acetone. The shape of the DLC bridge was observed by scanning electron microscope (SEM).

In order to measure the residual compressive stress of the film, thin (210μm thick) Si stripe of size 5mmX50mm were also used as the substrate. The curvature of the film-substrate composite was measured by the laser reflection method. The residual stress of the film was then calculated from the equilibrium equation of bending plate [7]. Nanoindentation was used to determine the hardness and the plane-strain modulus of 1 μm thick DLC film on Si substrate. The load-displacement curve was analyzed by Oliver and Pharr method [8]. In order to exclude the effect of the substrate, a maximum indentation load of 1mN was used to limit the maximum penetration depth to less than 10% of the film thickness. For the measurement of the elastic modulus by the sonic resonance method, the films of 2um in thickness were deposited on the Si (100) wafer of well-defined dimension (10mmX60mm). Details of the measurement were described elsewhere [9]. Flexural resonant frequency was measured by a sonic resonance system composed of driver and pickup transducers. The elastic property of thin film was obtained from the measured frequency by using the two layer composite model [9]. For the calculation, we assumed the Poisson's ratio of the film 0.3, since the obtained results were not sensitive to the values of the Poisson's ratio.

3. RESULTS AND DISCUSSION

The structure and properties of DLC films are strongly dependent on the kinetic energy of ions bombarding the film surface during growth. Since the ions in the capacitively coupled RF plasma are accelerated by the negative bias voltage, the kinetic energy of the ions is proportional to the self bias voltage of the cathode. We showed that the structure of DLC films deposited in the present experimental condition changed from polymer-like to diamond-like one with increasing negative bias voltage [10]. The film deposited at higher negative bias voltage is thus denser and harder with higher residual compressive stress. Fig. 2 shows the dependence of the residual compressive stress on the negative bias voltage. The residual compressive stress increased from 0.4 to 1.4GPa as the negative bias voltage increased from 100 to 550V. Hardness of the films also increased from 2.3 to 15.4GPa as measured by nanoindentation.

Fig. 3 shows typical microstructure of the DLC bridges obtained by the present method. The DLC film in Fig. 3 was deposited at the negative bias voltage of 400V. Since the DLC patch is much larger than the width of the bridges, etching the silicon oxide sacrificial layer could relieve the residual stress of only the DLC bridges by separating the bridge from the substrate. The length of the bridge was recovered to its unstressed one, while the ends were fixed by the DLC patches. As can be seen in Fig. 3, the center of the bridges was thus deformed upward resulting in sinusoidal

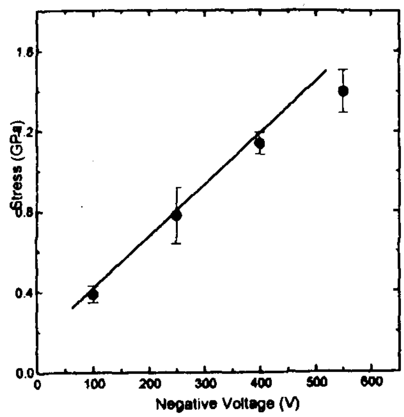

Fig.2. Dependence of residual compressive stress on the negative bias voltage.

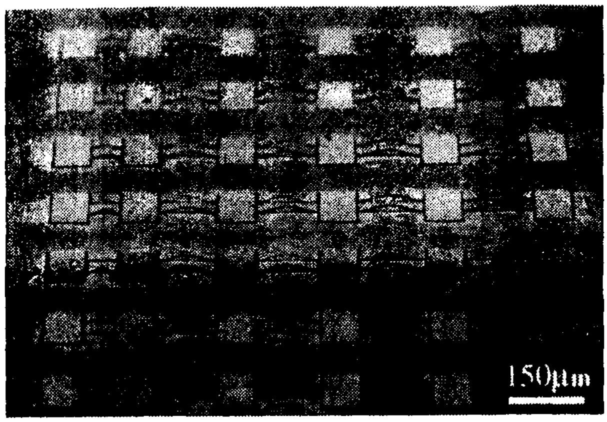

Fig. 3. Typical SEM microstrucuture of DLC bridges.

shape.

If the aspect ratio of the bridge length to the width is sufficiently large, the shape of the relieved bridge would be described by on dimensional buckling phenomena. Details of the theoretical analysis of the buckled thin film bridge

(1)

were previously reported [5]. The buckled film was balanced with the critical stress of buckling, σ_c. Hence, the stress strain relation of elastically isotropic thin film would be

$$\sigma_0 - \sigma_c = \frac{E}{(1-\nu)}\varepsilon$$

Here, σ_o is the residual compressive stress of the thin films. The average strain of the buckled film is given by

$$\bar{\varepsilon} = \left(\frac{\pi A_o}{\lambda}\right)^2, \qquad (2)$$

(1)

where ε is the strain of the buckled film, A_o the amplitude of the sinusoidal bridge and λ the length of the bridge. Hence, the biaxial elastic modulus of thin film is

$$\frac{E}{(1-\nu)} = (\frac{\lambda}{\pi A_o})^2(\sigma_o - \sigma_c). \qquad (3)$$

(1)

If the film thickness is much smaller than the amplitude as in the present case, the critical stress for buckling would be much smaller than the residual compressive stress [5], and Eq. (3) can be reduced

$$\frac{E}{(1-\nu)} \approx (\frac{\lambda}{\pi A_o})^2\sigma_o. \qquad (4)$$

(1)

This equation shows that the biaxial elastic modulus can be obtained by measuring the amplitude and the length of the bridge with known residual compressive stress. The amplitude of the bridge observed under SEM at the tilt angle of 80 degree.

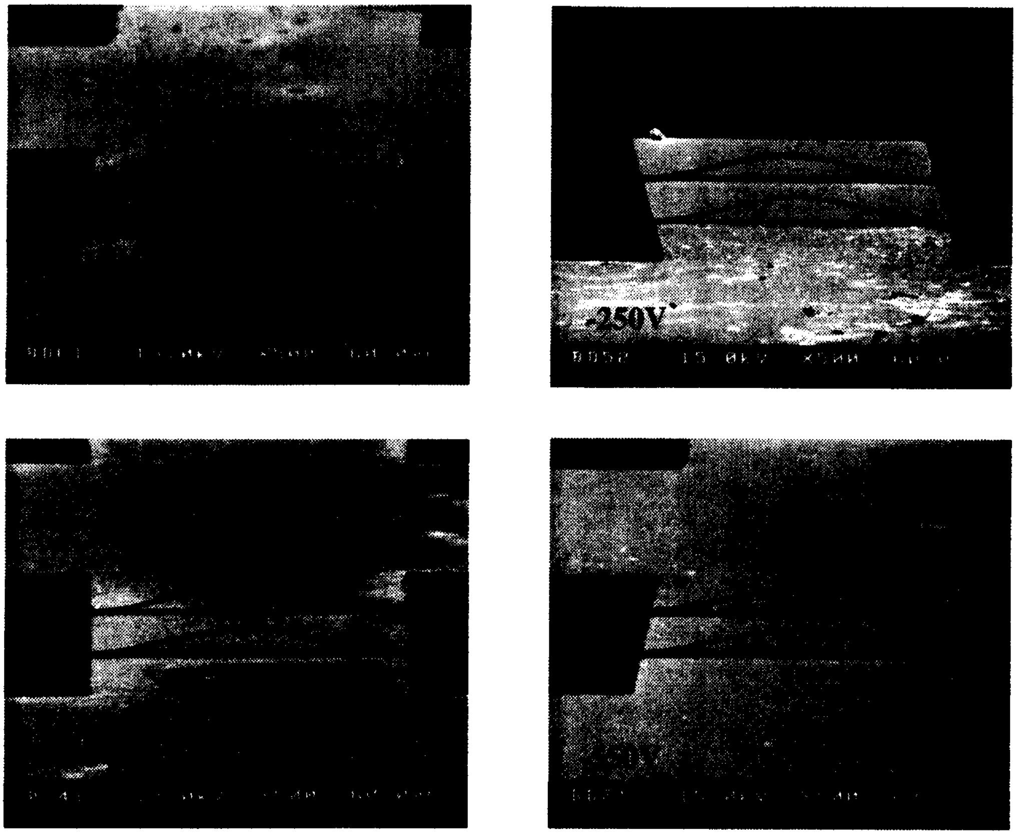

Fig. 4. SEM microstructure of DLC bridges at various negative bias voltage.

Fig. 4 shows SEM microstructures of the DLC bridges for various values of negative bias voltage. With increasing bias voltage, the amplitude of the bridge decreased. Since the residual stress increased with the bias voltage, this microstructural change illustrated that the elastic modulus of the film increased as the negative bias voltage increased. In the previous work [5], we investigated the effect of the film thickness and bridge length on the elastic modulus measurement. The measured values were independent of both the film thickness and the bridge length in the range of film thickness from 0.18 to 1.3μm and the bridge length from 60 to 150μm, respectively. It can be thus said that the present measurement is insensitive to the geometry of the bridge pattern, once the aspect ratio of the bridge length to the width is sufficiently large. Fig. 5 shows the dependence of the biaxial elastic modulus on the negative bias voltage at the constant film thickness of 1.3μm. As the negative bias voltage increased from 100 to 500V, the biaxial elastic modulus increased from 10 to 150GPa. This result is in good agreement with those of DLC films deposited by using PACVD method [11-13]. Depending on the deposition conditions, the values of E ranged from 90 to 220GPa and n from 0.22 to 0.39 [11-13].

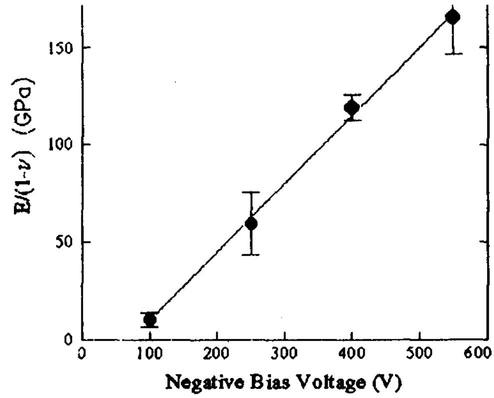

Fig. 5. Dependence of biaxial elastic modulus on the negative bias voltage

Fig. 6 (a) and (b) respectively shows the plane strain modulus measured by nanoindentation and Young's modulus measured by sonic vibration method. The same behaviors were observed as the negative bias voltage change as in the biaxial elastic modulus of Fig. 5. In order to compare the results in a quantitative manner, we assumed the Poisson's ratio of the films was 0.3, and calculated Young's modulus from biaxial elastic modulus and plane strain modulus. Table 1 summarized the calculated results. Nanoindentation and sonic vibration method results in the same values of Young's modulus in this experimental condition. However, the values obtained by the bridge method results in about 15GPa lower than those of other methods.

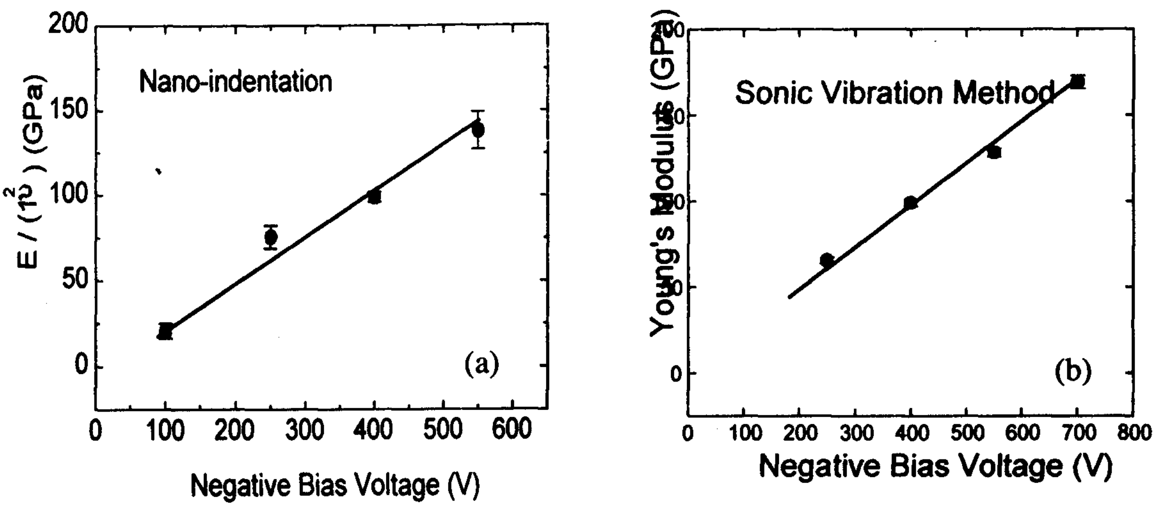

Fig.6 Elastic modulus measured by nanoindentation (a) and sonic vibration method (b).

Two possible reasons for this discrepancy can be addressed. First, during the oxygen plasma etching of DLC films for patterning, the plasma heating could affect the structure of DLC films. It has been well known that the structure and properties of DLC films are degraded by post-annealing at higher temperature [3]. It should be thus clarified the effects of oxygen plasma etching process on the properties of the DLC films, especially when the films contained high amount of hydrogen. Another reason would be the undercut of the patch occurred when SiO_2 layer was etched by BOE solution. Sinusoidal freehang of DLC films along the edge of the patch was clearly observed as in the Fig. 4 (c) and (d). Hence, the bridge length can be underestimated, resulting in the lower biaxial elastic modulus as can be seen in Eq. (4). The discrepancy would be thus removed by using lift off technology and etch stop formation, since the former will remove the oxygen plasma etching process and the latter will suppress the undercut problem. More elaborated micro-fabrication process is now under development.

Table 1 Calculated Young's modulus of DLC

V_b (V)	Nanoindentation (ν=0.3)	Sonic Vibration	Present Method (ν=0.3)
-100	19.1+5.6	-	6.9+1.3
-250	68.9±8.6	65.6±1.9	42.5±10.8
-400	90.2+3.7	99.1+2.2	86.8+21.3
-550	126.0±14.2	128.4±2.4	104.9±14.6

4. CONCLUSIONS

The elastic properties of DLC films were measured by producing DLC bridges which are free from mechanical constraint of substrate. Because of the high residual stress of the DLC films, the bridge deformed in a sinusoidal shape of one wavelength. By measuring the amplitude and the bridge length and using independently measured residual stress, we could obtain the biaxial elastic modulus. The biaxial elastic modulus of DLC films deposited by r.f.-PACVD using benzene increased from 10 to 150 GPa with increasing negative bias voltage from 100 to 550V. This increase is in good agreement with the changes in the film properties from polymeric to diamond-like one in the present bias voltage range [10]. The result was also consistent with the Young's modulus measured by nanoindentation and sonic vibration method, in qualitative manner. It can be concluded that the present method can be applied to measure the elastic properties of thin films. However, Young's modulus of the present method appeared smaller than those of other methods, due to the uncertainty in the bridge length due to undercut of DLC patches and possible damage of DLC films during oxygen plasma etching. More elaborate process for manufacturing the DLC bridges is in progress.

5. REFERENCES

1. N. Fujimori, New Diamond, **3** (1989) 20.
2. T. Imai, H. Nakahata, and N. Fujimori, US Patent 4,952,132 (1990).
3. J. C. Angus, P. Koidl, and S. Domitz, in: J. Mort, F. Jansen (Eds.), Plasma Deposited Thin Films, CRC, Boca Raton, FL, 1986, p. 89.
4. K.-R. Lee, Y.-J. Baik and K. Y. Eun, MRS Proc. **308** (1993) 101.
5. S.-J. Cho, K.-R. Lee, K. Y. Eun, J.-H. Jeong, D. Kwon, Diam. Rel. Mater., **8** (1999) 1067.

6. K.-R. Lee, Y.-J. Baik, and K. Y. Eun, Diam. Rel. Mater., **2** (1993) 910.
7. A. Brenner and S. Senderoff, J. Res. Natl Bor. Stand., **42** (1949) 105.
8. W. C. Oliver and G. M. Pharr, J. Mater. Res. **7** (1992) 1564.
9. K.-H. Cho and Y. Kim, J. Mater. Res. **14** (1999) 1996.
10. K.-R. Lee, Y.-J. Baik, K. Y. Eun and S. Han, Diam. Rel. Mater. **3** (1994) 1230.
11. M. A. Elkhakani, M. Chaker, A. Jean, S. Boily, J. C. Kieffer, M. E. O'Hren, M. F. Ravet, F. Rousseaux, J. Mater. Res., **9** (1990) 32.
12. X. Jiang, K. Riechelt, B. Stritzker, J. Appl. Phys., **68** (1990) 1018.
13. J. C. Pivin, Thin Solid Films, **229** (1993) 83.