# MEASUREMENT OF ELASTIC MODULUS AND POISSON'S RATIO OF DIAMOND–LIKE CARBON FILMS

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## ABSTRACT

Elastic modulus and Poisson's ratio of diamond–like carbon (DLC) film was measured by a simple method using DLC bridges which are free from mechanical constraint of substrate. The DLC films were deposited on Si wafer by $C_6H_6$ r.f. glow discharge at the deposition pressure 1.33 Pa. Because of the high residual compressive stress of the film, the bridge exhibited a sinusoidal displacement by removing the constraint of the substrate. By measuring the amplitude with known bridge length, we could determine the strain of the film required to adhere to the substrate. Combined with independent stress measurement by laser reflection method, this method allows calculation of the biaxial elastic modulus, $E/(1-\nu)$, where $E$ is the elastic modulus and $\nu$ Poisson's ratio of the DLC film. By comparing the biaxial elastic modulus with plane–strain modulus, $E/(1-\nu^2)$, measured by nano–indentation, we could further determine the elastic modulus and Poisson's ratio, independently. The elastic modulus, $E$, increased from 87 to 133 GPa as the negative bias voltage increased from 400 to 550 V. Poisson's ratio was estimated to be about 0.20 in this bias voltage range. For the negative bias voltages less than 400 V, however, the present method resulted in negative Poisson's ratio which is physically impossible. The limitation of the present method was also discussed.

## INTRODUCTION

High ratio of elastic modulus to mass density of diamond–like carbon (DLC) film has attracted much attention for the applications using high acoustic wave velocity. Among the applications are the overcoats for speaker diaphragm and surface acoustic wave devices [1, 2]. Accurate measurement of the elastic properties of the DLC film is the prerequisite for these applications. Elastic modulus of thin film is generally different from that of bulk materials mainly due to the defects or textures in the thin film structure. Furthermore, the properties of DLC film can be varied in wide range by changing the deposition condition [3]. It is thus desirable to measure the elastic properties of as deposited thin films. The elastic modulus of thin films have been measured by various methods, i.e. nano–indentation [4], Brillouin light scattering measurement [5], ultrasonic surface wave measurement [6], bulge test [7] or vibration membrane method [8]. However, these techniques need sophisticated instruments and analysis technique or delicate micro–machining process.

Recently, we suggested a simple method to measure the elastic modulus and Poisson's ratio of the DLC film deposited on Si wafer [9, 10]. This method involved etching a side of Si substrate using the DLC film as an etching mask. The etching process resulted in unstressed DLC freehang of sinusoidal shape. By measuring the amplitude and wavelength of the sinusoidal edge, it was possible to obtain the strain of the film. Because the residual stress of DLC film can be independently obtained by measuring the curvature of film/substrate composite, biaxial elastic modulus was thus calculated from a simple stress–strain relation of thin films [9, 10]. Although the technique was successful in measuring the elastic properties of DLC films, large uncertainties could be involved when measuring the wavelength and the amplitude. The uncertainties were more significant in the case of thin films of high elastic modulii where the DLC freehang exhibited small amplitude and large wavelength.

In the present work, we produced the DLC bridges between DLC patches by using a simple MEMS technology. Because the bridges were free from the mechanical constraint of the substrate, the shape of the bridge appeared sine wave of one wavelength which is equal to the bridge length. More accurate measurement of the sinusoidal displacement was thus possible even in the case of thin films of high elastic modulii. This technique was employed to measure the elastic properties of the DLC films deposited by r.f. PACVD method. We compare the measured elastic properties with those obtained by the previous method [9, 10].

Mat. Res. Soc. Symp. Proc. Vol. 518 © 1998 Materials Research Society

## EXPERIMENTAL METHOD

DLC films were deposited on $SiO_2$ sacrificial layer of thickness 0.5 $\mu$m which was grown by thermal oxidation on p type Si (100) wafer. 13.56MHz r.f. glow discharge of $C_6H_6$ was employed for the DLC film deposition. The deposition pressure was fixed at 1.33 Pa. However, the negative self bias voltage was varied in the range from 100 to 550 V by adjusting the supplied r.f. power. In order to measure the residual stresses of the films, thin (210±10 $\mu$m thick) Si stripes of size 5mm×50mm were also used as the substrate. The curvature of the film–substrate composite was measured by a laser reflection method. The residual stress of the film was then calculated from the equilibrium equation of bending plate [11]. Nano–indentation was used to determine the hardness and the plane–strain modulus of 1 $\mu$m thick DLC film on Si substrate. The load–displacement curve was analyzed by Oliver and Pharr method [4]. 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.

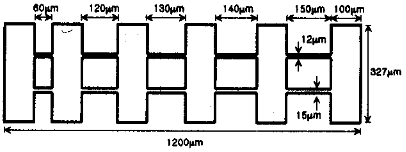

Figure 1 : Schematic of the bridge pattern.

The DLC films were patterned by a conventional lithography to obtain thin DLC bridges between 100$\mu$m×327$\mu$m DLC patch. 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 150$\mu$m and the width from 12 to 15 $\mu$m. Exposed DLC film was etched by oxygen plasma and the sacrificial $SiO_2$ layer was then removed by 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 bridges was observed by scanning electron microscope (SEM).

## RESULTS AND DISCUSSION

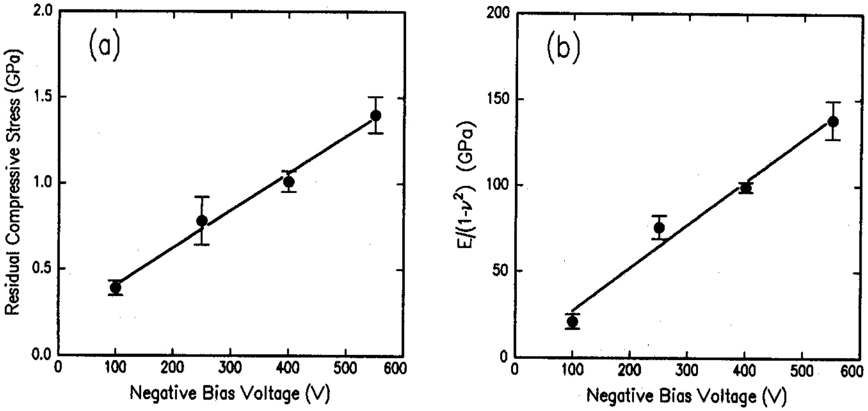

Figure 2 : Dependence of residual compressive stress (a) and plane–strain modulus (b) on the negative bias voltage.

The structure and properties of DLC films are strongly dependent on the kinetic energy of ions that bombard the film surface during growth [3]. Since the ions in the capacitively coupled r.f. plasma are accelerated by the negative self 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 this experimental condition changed from polymer–like to diamond–like one with increasing negative bias voltage [12]. The film deposited at higher negative bias voltage is thus denser and harder with high residual compressive stress. Fig. 2 shows the residual compressive stress measured by the curvature measurement method and plane–strain modulus, $E/(1-\nu^2)$, obtain by nano–indentation for various values of the negative bias voltages. As the negative bias voltage increased from 100 to 550 V, both the residual stress and the plane–strain modulus linearly increased. Hardness of the films measured by nano–indentation were also increased from 2.3 to 15.4 GPa with increasing negative bias voltage.

Fig. 3 shows typical microstructure of the DLC bridges obtained by the present method. The microstructure was obtained using the DLC film deposited at the negative bias voltage of 400 V and the pressure 1.33 Pa. Because the size of the DLC patch is much larger than the width of the DLC bridges, etching the $SiO_2$ sacrificial layer could relieve the residual stress of only the DLC bridges by separating the bridge from the substrate. Hence, the length of the bridge was recovered to its unstressed one, while the ends were still fixed by the DLC patches. As can be seen in Fig. 3, the center of the bridges were thus deformed upward resulting in sinusoidal shape. The deformed bridge corresponds to the one wavelength of the sinusoidal freehang in the previous work [9, 10]. In the present work, however, the wavelength could be controlled by the bridge length, which results in more accurate measurement of the amplitude and the wavelength. This major point would be more significant in the case of thin films of high elastic modulii.

If the aspect ratio of the bridge length to the width is sufficiently large, the shape of the relieved bridge would be describe by an one dimensional sinusoidal variation such as $y = A_o \sin(2\pi x/\ell)$. The unstressed length $\ell_o$ can be thus described by [13, 14]

$$\ell_o \approx \ell \left[ 1 + \left( \frac{\pi A_o}{\ell} \right)^2 \right]. \tag{1}$$

Here, $A_o$ is the amplitude and $\ell$ the bridge length. In general, the strain is given by the ratio of the change in length to the unstressed length. The strain $\epsilon$ is thus given by

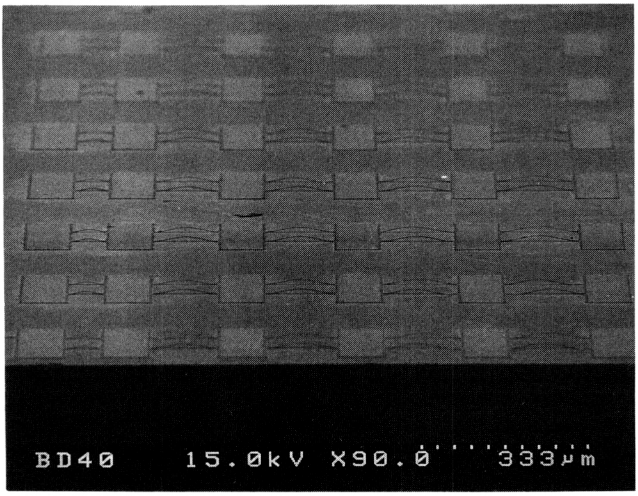

Figure 3 : Typical microstructure of DLC bridges. The film was deposited at the negative bias voltage of 400 V and the deposition pressure 1.33 Pa. The film thickness was 0.5 $\mu$m.

$$\epsilon = -\frac{\ell - \ell_o}{\ell_o} \approx \left(\frac{\pi A_o}{\ell}\right)^2. \tag{2}$$

The stress–strain relation for elastically isotropic films is

$$\sigma = \frac{E}{1-\nu}\epsilon, \tag{3}$$

where $\sigma$ is the residual stress, $E$ elastic modulus, $\nu$ Poisson's ratio of the film. By rearranging the Eq. (3) and substituting $\epsilon$ by Eq. (2), one can obtain

$$\frac{E}{(1-\nu)} = \left(\frac{\ell}{\pi A_o}\right)^2 \sigma. \tag{4}$$

The biaxial elastic modulus, $E/(1-\nu)$, can be thus obtained by measuring the amplitude and the length of the bridge with known residual compressive stress of Fig. 2 (a). The amplitude of the bridge was obtained from the deformation of the bridge observed under SEM at the tilt angle of 80°. Because the etching process also etch the $SiO_2$ layer under the DLC patch, it must be considered that the $\ell$ is not the bridge length of the mask pattern but the sum of the bridge length and the under-cut depth.

In order to investigate the effect of the film thickness on the elastic modulus measurement, we prepared the DLC bridges of various film thicknesses. As shown in Fig. 4 (a), the elastic modulii appeared independent of the film thickness in the range from 0.18 to 0.13 $\mu$m. This result can be compared with that of the previous study using DLC freehang of sinusoidal shape [9]. In the present work where the wavelength was fixed by the bridge length, the amplitude were observed to be constant regardless to the film thickness. In the previous work, however, both the amplitude and the wavelength increased with increasing film [9]. Large uncertainties could be thus involved in measuring the amplitude and the wavelength when the film thickness was small. Previous work reported that the biaxial elastic moduli were independent of the film thickness when the film is thicker than 0.2 $\mu$m. However, the biaxial elastic modulus of thin film (0.18 $\mu$m) was estimated to be smaller than those of larger films [9]. Fig. 4 (b) showed the biaxial elastic modulii for various values of the bridge lengths ranging from 60 to 150 $\mu$m. In this range of the bridge length, $E/(1-\nu)$ were estimated to be 115±5 GPa and independent of both the bridge length and the bridge width. 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.

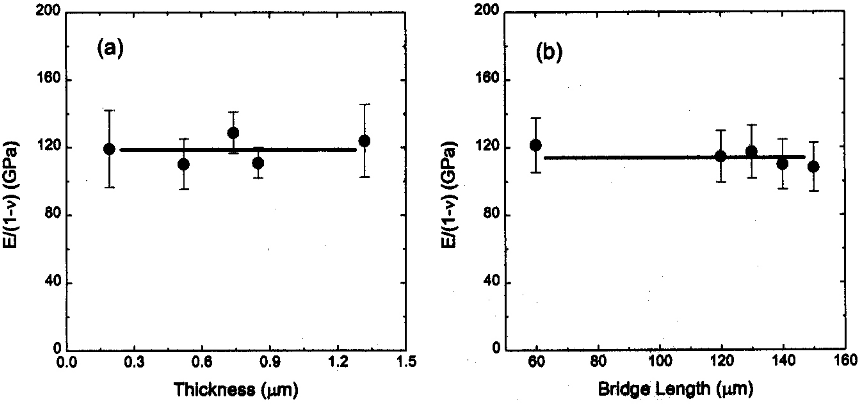

Figure 4 : Measured biaxial elastic modulus for various values of the film thicknesses (a) and the bridge lengths (b). The films were deposited at the negative bias voltage of 400 V and the deposition pressure 1.33 Pa.

Fig. 5 shows the dependence of the biaxial elastic modulus on the negative bias voltage. As the negative bias voltage increased from 100 to 550 V, the biaxial elastic modulus increased from 10 to 150 GPa. From the ratios of the plane–strain modulii measured by nano–indentation (Fig. 2 (b)) to the biaxial elastic modulii, we calculated Poisson's ratios and then obtained elastic modulii of the DLC films of various negative bias voltages. Table 1 summarized the calculated results. The elastic modulii increased from 16 to 128 with increasing negative bias voltage. However, negative values of Poisson's ratio were obtained when the bias voltage was low (100 and 250 V), which is physically impossible. The calculated values of the elastic modulus is thus highly uncertain in this bias voltage range. When the bias voltage was lower than 400 V, we showed that the deposited films are soft polymeric [12]. Even if the yield strengths of these films are unknown, the stress level can be higher than the yield strength of the film resulting in plastic deformation. Because the present technique is based on the assumption of elastic deformation, the mechanical properties of soft polymeric films would not be measured by the present method. When the negative bias voltage was higher than 400 V, we obtained positive Poisson's ratio. Because higher negative bias voltage results in dense diamond–like films [12], elastic deformation seems to occur in this range. The obtained values of elastic modulus and Poisson's ratio were in good agreement with the elastic properties of DLC films deposited by PACVD method [7, 15, 16]. Depending on the deposition conditions, the values of $E$ ranged from 90 to 220 GPa and $\nu$ from 0.22 to 0.39 [7, 15, 16].

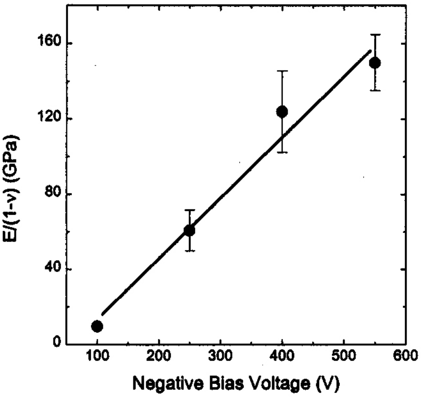

Figure 5 : Dependence of the biaxial elastic modulus on the negative bias voltage.

| Negative Bias voltage (V) | Elastic Modulus, $E$ (GPa) | Poisson's Ratio |
|---|---|---|
| 100 | 16±7* | -0.46±0.16 |
| 250 | 71±12* | -0.10±0.39 |
| 400 | 87±15 | 0.26±0.26 |
| 550 | 133±16 | 0.14±0.15 |

Table 1. Calculated elastic modulii and Poisson's ratios of DLC films deposited by r.f.–PACVD.

## 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 compressive stress of the DLC films, the bridge deformed in a sinusoidal shape of one wavelength. By measuring the amplitude and using independently measured bridge length and residual stress, we could obtain the biaxial elastic modulus. Because the wavelength was determined by the bridge length, the present method could eliminate the uncertainties in the wavelength measurement which were significant in the case of thin film of high elastic modulus. The elastic modulus of DLC films deposited by r.f.–PACVD using benzene increased from 87 to 133 GPa with increasing negative bias voltage from 400 to 550V. Poisson's ratio was estimated to be about 0.2 in this bias voltage range. However, the present method could not be applied to measure the properties of soft polymeric films of high residual stress where the plastic deformation can occur by the substrate etching process.

## ACKNOWLEDGEMENT

This work was financially supported by the Ministry of Science and Technology of Korea and the Korea Science and Engineering Foundation through the Center of Interface Science and Engineering of Materials at Korea Advanced Institute of Science and Technology.

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