Abstract

The elastic properties of diamond-like carbon (DLC) films were measured by a simple method using DLC bridges which are free from the mechanical constraints of the substrate. The DLC films were deposited on a Si wafer by radio frequency (RF) glow discharge at a deposition pressure of 1.33 Pa. Because of the high residual compressive stress of the film, the bridge exhibited a sinusoidal displacement on removing the substrate constraint. By measuring the amplitude with a known bridge length, we could determine the strain of the film which occurred by stress relaxation. Combined with independent stress measurement using the laser reflection method, this method allows the calculation of the biaxial elastic modulus, $E(1 - v)$, where $E$ is the elastic modulus and $v$ is Poisson’s ratio of the DLC film. The biaxial elastic modulus increased from 10 to 150 GPa with increasing negative bias voltage from 100 to 550 V. By comparing the biaxial elastic modulus with the plane-strain modulus, $E/(1 - v^2)$, measured by nano-indentation, we could further determine the elastic modulus and Poisson’s ratio, independently. The elastic modulus, $E$, ranged from 16 to 133 GPa in this range of the negative bias voltage. However, large errors were incorporated in the calculation of Poisson’s ratio due to the pile up of errors in the measurements of the elastic properties and the residual compressive stress.

1. Introduction

Diamond-like carbon (DLC) films, also called hydrogenated amorphous carbon films, have an unique combination of physical and chemical properties similar to diamond. The unusual combination of high hardness, wear resistance, optical transparency, chemical inertness and low friction coefficient, has motivated studies into various applications. A high ratio of elastic modulus to mass density of DLC film has also attracted much attention for applications using high acoustic wave velocity. Among the applications are the overcoats for speaker diaphragm and surface acoustic wave devices [1,2]. The elastic properties are also critical for the films in micro-electromechanical systems (MEMS). Accurate measurement of the elastic properties is the prerequisite for these applications.

Elastic modulus of thin film is generally different from that of the bulk materials mainly due to defects or textures of the films. Furthermore, the properties of DLC films can be varied over 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 properties of thin films have been measured by various methods: nano-indentation [4]; Brillouin light scattering measurement [5]; ultrasonic surface wave measurement [6]; bulge test [7] and the vibration membrane method [8]. However, these techniques need sophisticated instruments and analysis techniques or delicate micro-machining process.

In the present paper, we suggest a simple method to measure the elastic properties of the DLC films deposited on Si wafer. Typical DLC films have high residual compressive stress of up to 10 GPa [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 [9]. If one can measure the strain of the film required to adhere on the Si substrate,
biaxial elastic modulus would be thus obtained from a simple stress–strain relation of thin films. By comparing the biaxial elastic modulus with plane–strain modulus measured by nano-indentation, we could further obtain the elastic modulus and Poisson’s ratio, independently. Recently, we reported a method to measure the strain of DLC films during the residual stress relaxation [10,11]. The method involved etching a side of Si substrate using the DLC film as an etching mask, which resulted in unstressed DLC freehang sinusoidal in shape. It was possible to obtain the strain by measuring the amplitude and the wavelength of the sinusoidal edge. 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 difficulties were more significant in the case of thin films of high elastic moduli where the freehang exhibited small amplitude and large wavelength [10]. In the present work, we produced the DLC bridges between DLC patches using simple MEMS technology. Because the bridges were free from the mechanical constraint of the substrate, the shape of the bridge appeared with a 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 moduli. This technique was employed to measure the elastic properties of the DLC films deposited by radio frequency plasma assisted chemical vapour deposition (RF-PACVD).

2. Experimental

Glow discharge of 13.56 MHz was employed for the DLC film deposition. Details of the deposition equipment were described elsewhere [12]. The deposition pressure was fixed at 1.33 Pa. However, the negative self bombard the film surface during growth [3]. 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 were patterned by conventional lithography so as to obtain thin DLC bridges between 100 μm × 327 μm 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 150 μm and the width from 12 to 15 μm. The exposed DLC film was etched by oxygen plasma and the sacrificial SiO₂ layer was then removed by a 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 microscopy (SEM).

In order to measure the residual compressive stress of the film, thin (210 ± 10 μm thick) Si stripes were grown on Si(100) wafer by thermal oxidation. The DLC film was chemically so inert that we could not observe any surface damage or change in the film thickness.

In the present work, we produced the DLC bridges between DLC patches using simple MEMS technology. Because the bridges were free from the mechanical constraint of the substrate, the shape of the bridge appeared with a 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 moduli. This technique was employed to measure the elastic properties of the DLC films deposited by radio frequency plasma assisted chemical vapour deposition (RF-PACVD).

3. Results and discussion

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 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 were patterned by conventional lithography so as to obtain thin DLC bridges between 100 μm × 327 μm 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 150 μm and the width from 12 to 15 μm. The exposed DLC film was etched by oxygen plasma and the sacrificial SiO₂ layer was then removed by a 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 microscopy (SEM).

In order to measure the residual compressive stress of the film, thin (210 ± 10 μm thick) Si stripes were grown on Si(100) wafer by thermal oxidation. The DLC film was chemically so inert that we could not observe any surface damage or change in the film thickness.

In the present work, we produced the DLC bridges between DLC patches using simple MEMS technology. Because the bridges were free from the mechanical constraint of the substrate, the shape of the bridge appeared with a 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 moduli. This technique was employed to measure the elastic properties of the DLC films deposited by radio frequency plasma assisted chemical vapour deposition (RF-PACVD).
films deposited in the present experimental condition changed from polymer-like to diamond-like one with increasing negative bias voltage [14]. The film deposited at higher negative bias voltage is thus denser and harder with high residual compressive stress. Fig. 2 shows the dependencies of the residual compressive stress and the plane-strain modulus on the negative bias voltage. Both the residual stress and the plane-strain modulus monotonically increased as the negative bias voltage increased. Hardness of the films also increased from 2.3 to 15.4 GPa with an increasing negative bias voltage from 100 to 550 V.

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 400 V. Since the DLC patch is much larger than the width of the bridges, etching the SiO\(_2\) 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 were thus deformed upward resulting in sinusoidal shape. The deformed bridge corresponds to the one wavelength of the sinusoidal freehang in the previous work [10,11]. In the present work, however, the wavelength could be controlled by the bridge length, which resulted in more accurate measurement of the amplitude. This advantage was more significant in the case of thin films of high elastic moduli as will be discussed later.

If the aspect ratio of the bridge length to the width is sufficiently large, the shape of the relieved bridge would be described by one-dimensional buckling phenomena. Fig. 4 shows the schematic of the buckled thin film. Most of the residual stress, \(\sigma_0\), was relieved by removing the mechanical constraint of the substrate. However, the buckled film was balanced with remained stress in the film which is approximately equal to the critical stress of buckling, \(\sigma_c\), as shown by Evans and Hutchinson in the buckled wide column [15]. In the case of elastically isotropic thin films, the relieved stress, \(\sigma_0 - \sigma_c\), is thus given by product of the biaxial elastic modulus.
modulus, $E(1 - \nu)$ and the strain of the buckling, $\varepsilon_c$;  
\[ \Delta \sigma = \sigma_0 - \sigma_c = \frac{E}{1 - \nu} \varepsilon_c. \]  
(1)

From the momentum balance condition, the governing equation of the buckling is given by [16]:  
\[ D \frac{\partial^4 W}{\partial x^4} + \frac{\partial^2 W}{\partial x^2} = 0, \]  
(2)

where $D$ is the flexural rigidity, $E^2/12(1 - \nu^2)$, $W$ the displacement of the film in the $z$-direction and $t$ the film thickness. By solving Eq. (2) with the following boundary conditions:  
\[ W = \frac{\partial W}{\partial x} = 0 \]  
(3)
\[ W = \frac{\partial W}{\partial x} = 0 \]  
(4)

one can obtain the shape of the buckled film and the critical stress as following:  
\[ W(x) = A_s \left(1 + \cos \left(\frac{2\pi}{\lambda} x\right)\right), \]  
(5)
\[ \sigma_c = \frac{4\pi^2 D}{\lambda^2 t^3}. \]  
(6)

Since the displacement in the $x$ direction is negligible in buckling, the strain of the buckling is:  
\[ \varepsilon_c = \frac{1}{2} \left(\frac{\partial W}{\partial x}\right)^2. \]  
(7)

Hence, the average strain is obtained by:  
\[ \varepsilon_c = \frac{1}{\lambda} \int_0^{\lambda/2} \frac{1}{2} \left(\frac{\partial W}{\partial x}\right)^2 dx \]  
(8)
\[ = \frac{1}{\lambda} \int_0^{\lambda/2} \left(2\pi A_s / \lambda\right)^2 \sin^2 \left(\frac{2\pi}{\lambda} x\right) dx \]  
(9)
\[ = \left(\frac{\pi A_s}{\lambda}\right)^2. \]  
(10)

From Eq. (1) and (10), the biaxial elastic modulus can be expressed as:  
\[ E = \frac{1}{1 - \nu} \left(\frac{\lambda}{\pi A_s}\right)^2 (\sigma_0 - \sigma_c). \]  
(11)

On the other hand, from Eq. (6):  
\[ E = \frac{3(1 + \nu) \lambda^2}{t^3 \pi^2} \sigma_c. \]  
(12)

By combining Eqs. (11) and (12), one can obtain:  
\[ \frac{\sigma_c}{\sigma_0} = \frac{1}{1 + 3(1 + \nu)A_s/(\tau t)^2}. \]  
(13)

This result shows that the critical stress is much smaller than the residual stress when the film thickness is small compared to the deflection at the center of the buckled bridge. In the present experimental conditions, the values of $A_s$, $t$ and $\tau$ are in the order of 10. Hence, Eq. (11) can be simplified as:  
\[ E = \frac{1}{1 - \nu} \left(\frac{\lambda}{\pi A_s}\right)^2 \sigma_c. \]  
(14)

Eq. (14) 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 was obtained from the deformation of the bridge observed under SEM at the tilt angle of 80°. Because the etching process also etches the SiO$_2$ layer under the DLC patch, it must be considered that the $\lambda$ is not the bridge length of the mask pattern but the sum of the bridge length and the under-cut depth. The effect of the under-cut depth will be discussed later.

In order to investigate the effect of the film thickness on the elastic modulus measurement, we prepared DLC bridges of various film thicknesses at the constant negative bias voltage of -400 V. As shown in Fig. 5a, the biaxial elastic modulus were estimated to be 115 $\pm$ 5 GPa, which is independent of the film thickness in the range from 0.18 to 1.3 $\mu$m. This result can be compared with that of the previous study using DLC freehang of sinusoidal shape [10]. 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. On the other hand, both the amplitude and the wavelength increased with increasing the film thickness in the previous work [10]. 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 modulus of thin film (0.18 $\mu$m) was estimated to be smaller than those of thicker films [10]. Fig. 5b showed the biaxial elastic moduli for various values of the bridge lengths ranging from 60 to 150 $\mu$m. In this range of the bridge length, biaxial elastic modulii were 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. By considering the increased ratio of under-cut depth to the bridge length with decreasing the bridge length, we can also conclude that the effect of under-cut etching was negligible in the present measurement.

Fig. 6 shows the dependence of the biaxial elastic...
modulus on the negative bias voltage at the constant film thickness of 1.3±0.1 μm. 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 moduli measured by nano-indentation (Fig. 2b) to the biaxial elastic moduli of Fig. 6, we calculated Poisson’s ratios and elastic moduli of the DLC films for various negative bias voltages. Table 1 summarized the calculated results. The elastic moduli increased from 16 to 133 GPa with increasing negative bias voltage. However, large uncertainties in the Poisson’s ratio were incorporated in the calculated values. This is due to the pile up of the errors in three different measurements; residual stress, plane-strain modulus and biaxial elastic modulus. For more reliable data of Poisson’s ratio, therefore, one should be able to reduce the error of each measurement. In spite of the large uncertainties in Poisson’s ratio, the obtained elastic properties of the films deposited at the bias voltage of >400 V were in good agreement with those of DLC films deposited using the PACVD method [7,17,18]. Depending on the deposition conditions, the values of $E$ ranged from 90 to 220 GPa and $v$ from 0.22 to 0.39 [7,17,18].

When the bias voltage was <400 V, negative values of Poisson’s ratio were obtained. Negative Poisson’s ratio is unusual but not unknown such as in iron pyrites, chromium and some polymers [19]. However, it must be also noted that when the bias voltage was <400 V, the deposited films are soft polymeric [14]. 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 present method may not be employed for the soft polymeric films of high residual stress.

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 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

![Fig. 5. 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 a deposition pressure of 1.33 Pa.](image)

![Fig. 6. Dependence of the biaxial elastic modulus on the negative bias voltage.](image)

![Table 1](image)
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 of the freehang method which were significant in the case of thin film of high elastic modulus [10,11]. The biaxial elastic modulus of DLC films deposited by RF-PACVD using benzene increased from 10 to 150 GPa with increasing negative bias voltage from 100 to 550 V. This increase is in good agreement with the changes in the film properties from polymeric to diamond-like one in this bias voltage range [14]. We also calculated the elastic modulus and Poisson’s ratio by comparing the biaxial elastic modulus with plane-strain modulus obtained by nano-indentation. Because of the pile up of errors in the measurements, the calculation resulted in large uncertainties. It is thus necessary to reduce the errors in the measurements to get more reliable data of Poisson’s ratio.

Acknowledgements

This work was financially supported by the Ministry of Science and Technology of Korea. Partial support from the Korea Science and Engineering Foundation through the Center for Interface Science and Engineering of Materials at the Korea Advanced Institute of Science and Technology is gratefully acknowledged.

References