A METHOD FOR INDEPENDENT MEASUREMENT OF ELASTIC MODULUS AND POISSON'S RATIO OF DIAMOND–LIKE CARBON FILMS

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ABSTRACT

A simple method to measure the elastic modulus and Poisson's ratio of diamond–like carbon (DLC) films deposited on Si wafer was suggested. This method involved etching a side of Si substrate using the DLC film as an etching mask. The edge of DLC overhang free from constraint of Si substrate exhibited periodic sinusoidal shape. By measuring the amplitude and the wavelength of the sinusoidal edge, we can 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 ν Poisson's ratio of the DLC films. 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. This method was employed to measure the mechanical properties of DLC films deposited by C_6H_6 r.f. glow discharge at the deposition pressure 1.33 Pa. The elastic modulus, E, increased from 94 to 128 GPa as the negative bias voltage increased from 400 to 550 V. Poisson's ratio was estimated to be about 0.22 in this bias voltage range. For the negative bias voltages less than 400 V, however, the present method resulted in negative Poisson's ratio. The limitation of the present method was 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 film is the prerequisite for these applications. Elastic modulus of thin film is generally different from that of the 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.

In the present work, we suggest a simple method to measure the elastic modulus and Poisson's ratio of the DLC film deposited on Si wafer. Typical DLC film has high residual compressive stress of up to 10 GPa. Although the residual stress is one of the major reasons for poor adhesion, we could use the residual stress to measure the elastic properties. By using an anisotropic etching technique, the side of Si substrate was etched with controlled etching depth. Since the DLC film is chemically inert, the etching process resulted in unstressed DLC freehang of sinusoidal shape. Measuring the amplitude and wavelength of the unstressed DLC freehang allowed us to find the strain of the DLC film required to adhere to the Si substrate. Because the residual stress of DLC film can be independently measured by the laser reflection method [9], biaxial elastic modulus was thus calculated from a simple stress–strain relation of thin films. Similar technique was used to measure the residual stress of SiO_2 or polycrystalline Si films on Si wafer by assuming the elastic modulii of the films equal to those of the bulk materials [10, 11]. 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.

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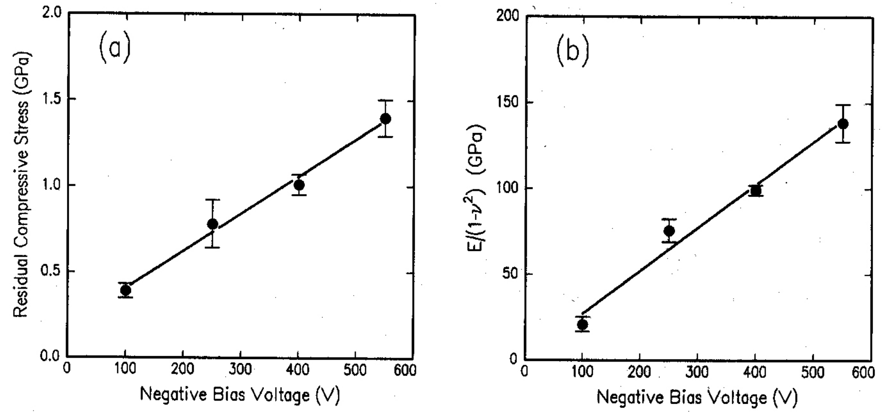

Figure 1: Dependence of residual compressive stress (a) and plane–strain modulus (b) on the negative bias voltage.

EXPERIMENTAL METHOD

DLC films were deposited on p type Si (100) wafer by using capacitively coupled r.f. glow discharge of C_6H_6. Details of the deposition condition were described elsewhere [9]. The films were deposited at a deposition pressure of 1.33 Pa. Negative self bias voltage was controlled in the range from 100 to 550 V by adjusting the r.f. power. In order to measure the residual stresses of the films, thin (100 ± 10 or 210 ± 10 μm 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 [12]. Nano–indentation 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 [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.

The DLC coated Si wafers were cleaved along <011> direction. The Si substrates of the samples were etched in the diluted KOH solution (5.6 mol/ℓ) at 70°C for 10 – 120 min. In order to obtain a uniform etching condition, the solution was agitated during the etching process. Because of the anisotropic etching rate of KOH solution, <011> direction of {111} plane of the Si substrate was remained as an etching front. DLC film is 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 samples were then dried in ambient air to prevent any damage by blowing dry nitrogen. The edge of the film freehang exhibited periodic sine wave. Scanning electron microscope (SEM) end–on view was used to measure the amplitude and the wavelength of the sinusoidal edge.

RESULTS AND DISCUSSION

Fig. 1 shows the residual compressive stresses (Fig. 1 (a)) and plane strain modulii (Fig. 1 (b)) of the DLC films measured by laser reflection method and nano–indentation, respectively. Both the residual stress and the plane strain modulus linearly increased as the negative bias voltage increased from 100 to 550 V.

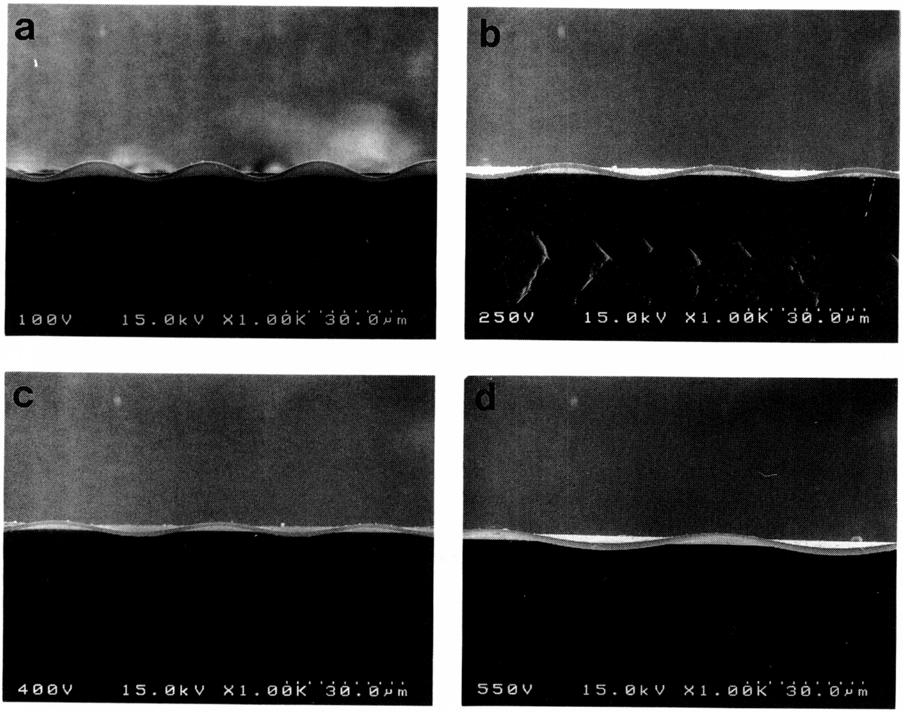

Figure 2: SEM end–on view of etched samples deposited at various negative bias voltages.
(a) −100 V (b) −250 V (c) −400 V (d) −550 V

Hardnesses of the samples measured by nano–indentation were also increased from 2.3 to 15.4 GPa with the negative bias voltage. The structure and properties of DLC films are strongly dependent on the kinetic energy of the particles that bombard the film surface [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 bias voltage. 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 [13]. The film deposited at higher negative bias voltage thus exhibits higher hardness and elastic modulus with higher residual stress.

The present etching process relieved the residual stress of the film by removing the constraint of the Si substrate. Hence, the edge of the film freehang was recovered to its unstressed length, resulting in the sinusoidal deformation. The sinusoidal shape of the film freehang edge is evident in SEM end–on views of the etched samples as shown in Fig. 2. In most cases, the sinusoidal edge extended more than 10 wavelengths without breaking the film. By measuring the unstressed freehang length for one wavelength, one can determine the strain of DLC films required to adhere on the Si substrate.

Assuming that the deformation tangential to the film edge is much more significant than that perpendicular to the edge, one can treat the deformation in one dimension. This assumption can be met if the freehang length is much larger than the etching depth. In the present work, ratio of the freehang length to the etching depth was in the order of 100. As shown in Fig. 2, the shape of the overhang edge can be described by a sinusoidal variation such as $y = A_o \sin(2\pi x/\lambda)$, where A_o is the amplitude and λ the wavelength. When the amplitude of the sinusoidal overhang is much smaller than the wavelength ($A_o \ll \lambda$), the unstressed length ℓ_o for one wavelength can be described by [10, 11]

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

In general, the strain is given by the ratio of the change in length to the unstressed length. The strain ϵ for one wavelength is thus given by

$$\begin{aligned} \epsilon &= -\frac{\lambda - \ell_o}{\ell_o} \qquad (2) \\ &\approx \left(\frac{\pi A_o}{\lambda} \right)^2. \qquad (3) \end{aligned}$$

The stress–strain relation for elastically isotropic films is

$$\sigma = \frac{E}{1-\nu}\epsilon, \tag{4}$$

where σ is the residual stress, E elastic modulus, ν Poisson's ratio of the film. By rearranging the Eq. (4) and substituting ϵ by Eq. (3), one can obtain

$$\frac{E}{(1-\nu)} = \left(\frac{\lambda}{\pi A_o} \right)^2 \sigma. \tag{5}$$

Eq. (5) shows that the biaxial elastic modulus $E/(1-\nu)$ can be obtained by measuring the amplitude and the wavelength of the sinusoidal freehang. In our previous paper, we reported the effects of the etching depth and the film thickness on the measurement by the present method [14]. It was shown that the results are not affected by the etching depth, once the etching depth is larger than about 10 μm. With increasing the film thickness, both the wavelength and the amplitude increased. However, the value of λ/A_o was kept constant when the thickness was larger than 0.2 μm. In the present work, the etching depth and the film thickness were thus controlled to be larger than 10 μm and 0.2 μm, respectively.

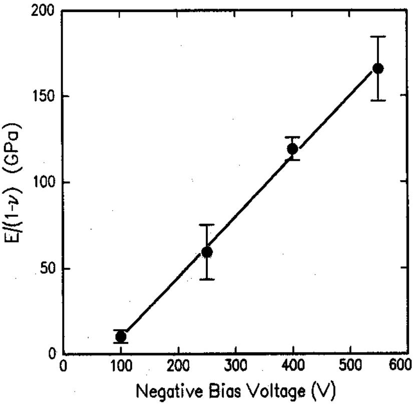

Figure 3. Dependence of the biaxial elastic modulus on the negative bias voltage.

Using the amplitude and the wavelength measured in Fig. 2 and the residual compressive stress of Fig 1 (a), we calculated the biaxial elastic modulii of the films. Fig. 3 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 166 GPa. From the ratios of the plane–strain modulii measured by nano–indentation 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 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 ones [13]. Hence, the stress level can be higher than the yield strength of the film resulting in plastic deformation. Even if the yield strength of these films are unknown, the microstructure of Fig. 2 (a) shows large deformation that can be in plastic region. 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. The negative Poisson's ratio in the soft films seems to result from this limitation. 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 [13], elastic deformation seems to occur in this range. The obtained values of elastic modulus and Poisson's ratio were in good agreement with the previous results on the mechanical properties of DLC films deposited by PACVD method. Depending on the deposition conditions, the values of E ranged from 90 to 220 GPa and ν from 0.22 to 0.39 [7, 15, 16].

Negative Bias voltage (V)	Elastic Modulus, E (GPa)	Poisson's Ratio
100	16±8*	-0.47±0.2
250	70±13*	-0.20±0.2
400	94±6	0.21±0.1
550	128±21	0.22±0.2

Table 1. Calculated elastic modulii and Poisson's ratios of DLC films deposited by r.f.–PACVD.
* Elastic modulus was obtained from the plain–strain modulus.

CONCLUSIONS

The present work showed that the elastic properties of DLC films could be measured by a simple method where the Si substrate was etched using the DLC film as an etching mask. Edge of the unstressed DLC freehang showed sinusoidal deformation. The biaxial elastic modulus was obtained from the stress–strain relation of thin films by the amplitude and the wavelength of the film freehang edge and the residual compressive stress that can be measured by an independent method. By combining this technique with nano–indentation, the elastic modulus and Poisson's ratio could be independently obtained. The elastic modulus of DLC films deposited by r.f.–PACVD using benzene increased from 94 to 128 GPa with increasing negative bias voltage from 400 to 550V. Poisson's ratio was estimated to be about 0.22 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.

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