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Biaxial elastic modulus of very thin diamond-like carbon (DLC) films

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Abstract

The biaxial elastic modulus of very thin diamond-like carbon (DLC) films was measured by the recently suggested free overhang method. The DLC films of thickness ranging from 33 to 1100 nm were deposited on Si wafers by radio frequency plasma-assisted chemical vapor deposition (r.f.-PACVD) or by the filtered vacuum arc (FVA) process. Because the substrate was partially removed to obtain sinusoidal free overhang of the DLC film, this method has an advantage over other methods in that the measured value is not affected by the mechanical properties of the substrate. This advantage is more significant for a very thin film deposited on a substrate with a large difference in mechanical properties. The measured biaxial elastic moduli were reasonable values as can be judged from the plane strain modulus of thick films measured by nanoindentation. The biaxial elastic modulus of the film deposited by r.f.-PACVD was 90 ± 3 GPa and that of the film deposited by FVA process was 600 ± 50 GPa. While the biaxial elastic modulus of the film deposited by FVA is independent of the film thickness, the film deposited by r.f.-PACVD exhibited decreased elastic modulus with decreasing film thickness when the film is thinner than 500 nm. Although the reason for the different behavior could not be clarified at the present state, differences in structural evolution during the initial stage of film growth seem to be the reason.

Keywords: Elastic modulus; Diamond-like carbon; Thickness dependence; Free overhang method

1. Introduction

As the requirement for thin films of thickness considerably less than 1 μm increases in various industrial applications, the mechanical properties of thin films become increasingly important for the reliability of devices. For example, the protective layer for a hard disk of large storage capacity should be less than 5 nm due to the reduced magnetic spacing between the magnetic layer and the read/write head [1]. The mechanical properties of the protective layer are, thus, one of the major concerns in the development of hard disks. The mechanical stability of low dielectric constant materials for large scale integrated circuits is also one of the critical factors to the implementation of high performance metallization [2,3]. However, the characterization of the mechanical properties of extremely thin films is often an unresolved problem. In diamond-like carbon (DLC) films, which have been considered as a candidate material for the above applications, the me-

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chanical properties of the films drastically vary with three dimensional interlinks enhanced by the sp^3 hybridization bond. Therefore, the mechanical properties are also useful to help identify their chemical bond structure.

Many methods have been suggested to measure the mechanical properties of thin films. Nanoindentation is the most widely used method to measure the hardness and elastic modulus of thin films [4]. However, the difficulties of nanoindentation for very thin films arise from high sensitivity to the substrate, especially when applying to a system where there is a large difference in mechanical properties between the substrate and film. The substrate effect is more significant in measuring the elastic modulus than in measuring the hardness, because the elastic behavior during unloading is dominated by the elastic behavior of the substrate (one should note that the elastic strain field is much wider than the plastic strain field). Furthermore, the effect of truncated indenter tip should be carefully considered for the analysis of shallow indentation [5]. Other methods using the propagation behavior of long wavelength acoustic phonon have also been employed for measuring elastic modulus [6–8]. However, these methods need sophisticated instrumental and analytical techniques to be applied to very thin films. The difficulties also arise from the separation of the acoustic signal of the thin film from the mixed signal of the thin film and the substrate.

Recently, we suggested a simple method to measure the elastic modulus of a DLC film, which has a compressive residual stress [9,10]. The residual stress can be estimated from the curvature of the film/substrate composite. Measuring the strain of the film required adherence onto the substrate, thus, enabling us to calculate the biaxial elastic modulus of DLC film from a simple stress–strain relation of thin films. The suggested method involves chemical etching of the substrate to evaluate the strain. The etching process produces an unstressed free overhang or bridge of sinusoidal shape. By measuring the amplitude and wavelength of the sinusoidal deformation, the strain of the film could be obtained. This method, successfully applied to measure the elastic moduli of DLC films [9,10], has an important advantage for very thin films. Because the substrate is completely excluded from the measurement process, the substrate does not affect the measured value.

In the present work, we applied the method to characterize very thin DLC films deposited by radio frequency plasma assisted chemical vapor deposition (r.f.-PACVD) or filtered vacuum arc (FVA). We used the unstressed free overhang to measure strain due to the ease of sample preparation. The present method resulted in reasonable values of elastic modulus, even if the investigated films had a wide range of mechanical properties. We observed a decrease of elastic modulus in DLC films of thickness < 500 nm, which were deposited by r.f.-PACVD. On the other hand, the films deposited by FVA showed a fixed elastic modulus in the range of film thickness from 33 to 650 nm.

2. Experimental

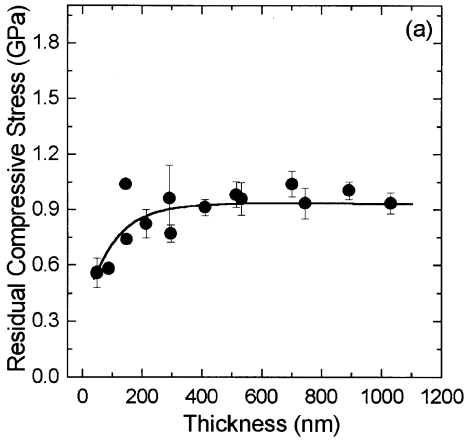
DLC films were deposited on p-type Si (100) wafers by using capacitively coupled r.f. glow discharge of C_6H_6 or a filtered vacuum arc of graphite. In r.f.-PACVD, the films were deposited at a negative bias voltage of 400 V and a deposition pressure of 1.33 Pa. Because these films have a high content of hydrogen, the films are also referred to as hydrogenated amorphous carbon (a-C:H) [11]. In the FVA process, the films were deposited using a CAF-45XY arc gun from the Commonwealth Scientific Corporation. During the deposition, the substrate was biased at -50 V and the deposition pressure was maintained at 7×10^3 Pa. Because of a high ionization ratio with optimum ion energy for dense carbon film deposition, the films deposited by FVA had a high content of sp^3 hybridized carbon bonds. These films, termed tetrahedral amorphous carbon (ta-C), have a high atomic density and hardness. The hardness of the films was measured by nanoindentation. In order to reduce the substrate effect on the hardness measurement, we used films of thickness > 500 nm on a Si (100) wafer. The hardness of the a-C:H films deposited by r.f.-PACVD (11 GPa) is much lower than that of ta-C films (45 GPa) because of the higher content of polymeric component and hydrogen [12]. Two classes of DLC film were selected to investigate the feasibility of the present method for a wide range of mechanical properties. The film thickness was varied from 33 nm to 1.1 μm by adjusting the deposition time. In order to measure the residual stress of the film, thin (100 ± 5 or 200 ± 5 μm in thickness) Si strips of 5×50 mm^2 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 the bending plate [13].

The DLC coated Si wafers were cleaved along the ⟨011⟩ direction. The Si substrates of the samples were etched in diluted KOH solution (5.6 mol/l) at 70°C for 1–120 min. In order to obtain a uniform etching condition, the solution was agitated during the etching process. Because of the anisotropic etching rate of Si in KOH solution, the ⟨011⟩ direction of the {111} plane of the Si substrate was maintained as an etching front. The DLC film is chemically so inert that we could not observe any surface damage or change in film thickness after the etching process. The etched samples were wet cleaned in sequence using deionized water, methanol

and acetone. The samples were then dried in ambient air to prevent any damage by blowing dry nitrogen. The shape of the free overhang and the etching depth were observed by scanning electron microscope (SEM). The edge of the free overhang appeared to be a continuous and periodic sinusoidal wave. A SEM end-on view at a tilt angle of 80° was used to measure the amplitude and wavelength of the sinusoidal edge.

3. Results and discussion

Fig. 1 shows the residual compressive stress for various film thicknesses. As shown in Fig. 1a, a-C:H films showed a fixed value for residual compressive stress (0.9 ± 0.1 GPa) when the film is thicker than 300 nm. However, a significant decrease in residual compressive stress was observed when the film was thinner than 300 nm. Fig. 1b shows the dependence of residual compressive stress of ta-C films on film thickness. In contrast to the a-C:H films, the ta-C films had a constant value for residual compressive stress (4.5 ± 0.2 GPa) regardless of film thickness. Fig. 2 shows the typical microstructure of a DLC free overhang obtained by the present method. Because the mechanical constraint of the substrate was removed by the etching process, the length of the free overhang edge was recovered to its unstressed one resulting in periodic sinusoidal deformation. Comparison of Fig. 2a,b shows that the sinusoidal deformations display the same behavior, even if the dimensions of the amplitude and wavelength were strongly dependent on the film thickness. The sinusoidal edge extended more than 10 wavelengths without breaking the film. Assuming that the deformation tangential to the film edge is much larger than that perpendicular to the edge, the elastic deformation can be treated in one dimension. This assumption can be



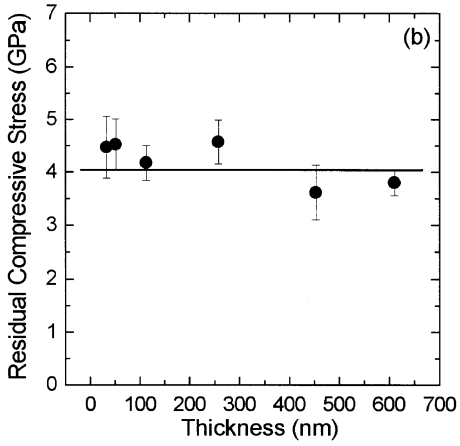


Fig. 1. Dependence of the residual compressive stress on film thickness: (a) a-C:H film deposited by r.f.-PACVD; and (b) ta-C film deposited by FVA.

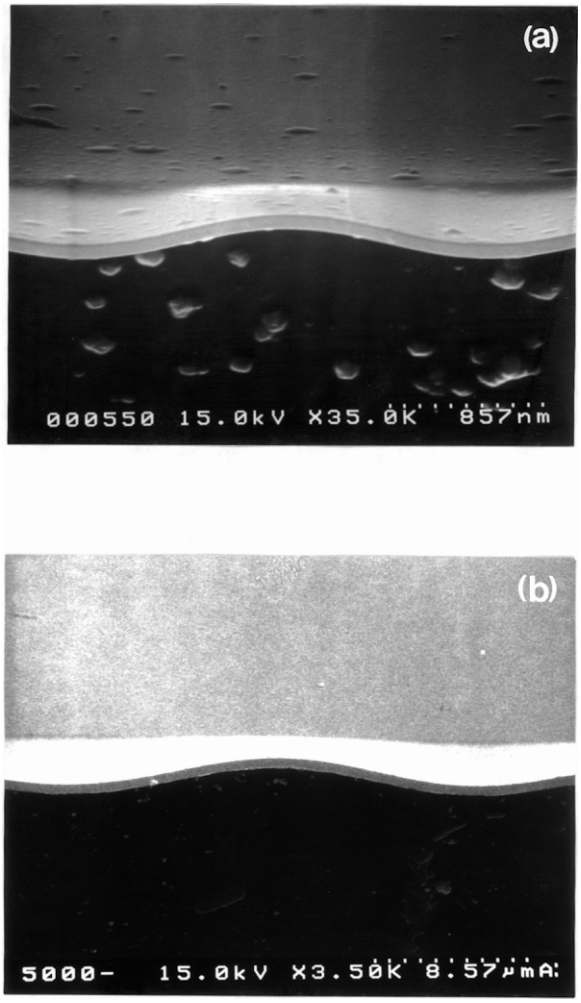


Fig. 2. Typical microstructure of the free overhang of the film deposited by r.f.-PACVD: (a) the film thickness is 55 nm and the etching depth = 2 μm; and (b) the film thickness is 546 nm and the etching depth = 11 μm.

met if the length of the continuous free overhang is much larger than the etching depth.

Cho et al. reported the elastic analysis of the unstressed free overhang or bridges [9,10]. Most of the residual stress, σ_0, was relieved by removing the mechanical constraint of the substrate. However, the free overhang was balanced with residual stress in the film, which is approximately equal to the critical stress of buckling, σ_c. From the stress–strain relationship for elastically isotropic thin films, the biaxial elastic modulus $E/(1-\upsilon)$, is thus given by

$$\frac{E}{1-\upsilon} = \frac{(\sigma_0 - \sigma_c)}{\bar{\varepsilon}} \tag{1}$$

where $\bar{\varepsilon}$ is the average strain of the film required to adhere to the substrate. From the one-dimensional buckling theory, the average strain can be expressed in terms of the ratio of the amplitude to the wavelength of the unstressed free overhang:

$$\bar{\varepsilon} = \left(\frac{\pi A_0}{\lambda}\right)^2. \tag{2}$$

Here, A_0 is the amplitude and λ, the wavelength of the free overhang. If the film thickness is much smaller than the amplitude, the critical stress of the buckling is negligible compared to the residual stress [10]. The biaxial elastic modulus is, thus, given by

$$\frac{E}{1-\upsilon} \approx \left(\frac{\lambda}{\pi A_0}\right)^2 \sigma_0. \tag{3}$$

This equation shows that the biaxial elastic modulus can be obtained by measuring the amplitude and wavelength of the free overhang for a film with known residual compressive stress.

Fig. 3 exhibits the typical change in A_0/λ values with etching depth. The data were obtained with a-C:H film of thickness 546 nm. The behavior can be divided into three regions as indicated in Fig. 3. In region I (small etching depth), the sinusoidal free overhang is not well developed due to insufficient stress relaxation. In region III (large etching depth), on the other hand, continuous and periodic sinusoidal free overhang could not be maintained due to the collapse of the large free overhang. The values of A_0/λ in these regions are, thus, meaningless for the elastic modulus calculation. In region II, continuous periodic sinusoidal free overhang could be observed resulting in a fixed value of A_0/λ, regardless of etching depth. The value in region II was selected for elastic modulus calculation. It was observed that both boundaries of the regions shifted to a smaller etching depth as the film thickness decreased.

Fig. 4 shows the biaxial elastic moduli of a-C:H films of various film thicknesses. In Fig. 4, the elastic moduli

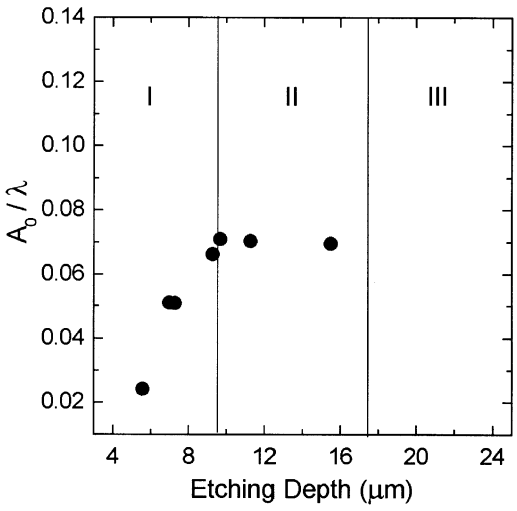


Fig. 3. Typical values of A_0/λ for various etching depths. The data were obtained with a film of thickness equal to 546 nm deposited by r.f.-PACVD.

obtained in films deposited on different substrates are also included. The elastic moduli of the films thicker than 500 nm were 90 ± 3 GPa. This value can be compared with the plane strain modulus, $E/(1-\upsilon^2)$, of the film measured by nanoindentation. In order to reduce the substrate effect, we used the film of thickness = 1 μm, for the nanoindentation measurement. The plane strain modulus obtained by analyzing the unloading behavior of the load–displacement curve was 75 ± 5 GPa. Although Poisson's ratio of the a-C:H film is not known, the elastic modulus, E, was estimated to be 66 ± 4 GPa in both cases if the Poisson's ratio was assumed to be 0.3. It can be, thus, said that the present method reports a reasonable value of the elastic modulus.

When the film was thinner than 500 nm, however, the elastic modulus of a-C:H film monotonically de-

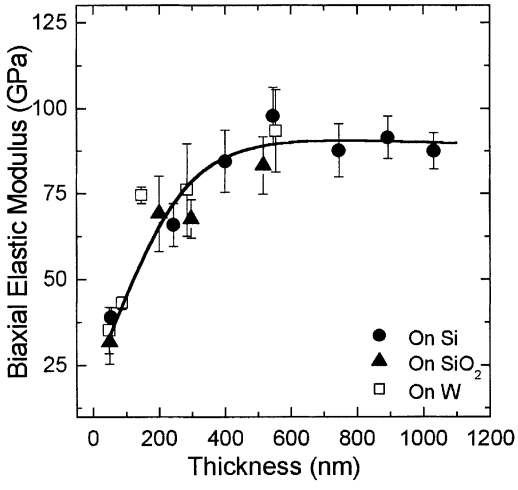


Fig. 4. Calculated biaxial elastic modulii of a-C:H films for various film thicknesses and substrate materials.

creased to 35 GPa as the film thickness decreased. Because the substrate is not involved in the present measurement, this decreasing behavior is not due to the substrate. Furthermore, the elastic modulus of Si ($E = 130.2$ GPa for Si (100) [14]) is approximately two times larger than that of the a-C:H film of the present work. Two possible reasons for the decreasing elastic modulus of very thin film could be suggested. As shown by in-situ XPS analysis during DLC film growth, a few nanometer thick interfacial reaction layer was formed at the initial stage of the deposition [15]. In the present work, Auger analysis of the free overhang also showed that the Si-C interfacial reaction layer was involved in the bottom surface of the free overhang. The effect of the interfacial reaction layer can be significant when measuring the properties of a very thin film. In order to investigate the effect of the interfacial reaction layer, we measured the elastic properties of the films deposited on SiO_2/Si and W/Si substrates. The films deposited on different substrate would have a different interfacial reaction layer. If the interfacial layer significantly affected the measured elastic modulus, a different behavior of the elastic modulus on the film thickness would be observed. However, Fig. 4 shows a similar behavior for the elastic modulus with film thickness regardless of the substrate materials. It can, thus, be said that the reason for the decrease in elastic modulus of very thin films is not due to the interfacial reaction layer.

A second reason would be the inhomogeneous film structure during the early stages of growth. The structural change during film growth was observed via the Raman spectra obtained for various film thicknesses. The Raman spectrum analysis for DLC films includes deconvolution of the spectrum with two Gaussian peaks; the G- and D-peak [16]. It is empirically known that the G-peak position illustrates the changes in atomic bond structure of the film. For example, structural changes during annealing of DLC films are correlated with the G-peak position shift to a higher wave number [17]. Fig. 5 shows the G-peak position for various film thicknesses. It is interesting to note that the G-peak position shows the same dependence on film thickness as that of elastic modulus (Fig. 4). When the film thickness is < 500 nm, the G-peak position monotonically shifted to a lower wave number. This result shows that the decrease in elastic modulus of the very thin film could be related to a structural change in the films. However, more careful investigation is required for definitive evidence of a structural change in this range of film thickness. It must also be noted that the G-peak position can be affected by the residual stress of the film. Further investigation of the film structure is in progress using high resolution TEM electron energy loss spectroscopy (EELS).

In contrast to a-C:H film, a decrease in the elastic

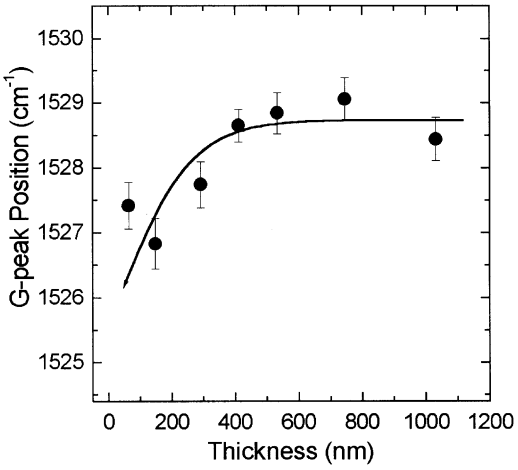


Fig. 5. Dependence of the G-peak position of Raman spectroscopy on the a-C:H film thickness.

modulus of very thin films was not observed in ta-C film. Fig. 6 shows the biaxial elastic modulii of ta-C films for various film thicknesses. A constant value of the elastic modulus of 600 ± 50 GPa was obtained in this range of film thickness. Assuming that the mechanical property changes in thin films is due to structural evolution during the early stages of growth, this result shows that structural evolution is strongly dependent on the deposition process. The elastic modulus of ta-C films obtained by the present method can be compared with those obtained by the nanoindentation method. Fig. 7 shows the results of continuous stiffness measurements (CSM) of the plane strain modulus. The results of two ta-C films of various film thicknesses of 610 and 125 nm were compared in Fig. 7. Because of large differences in mechanical properties between the ta-C film and Si substrate, a significant substrate effect was observed. The measured elastic modulus showed a

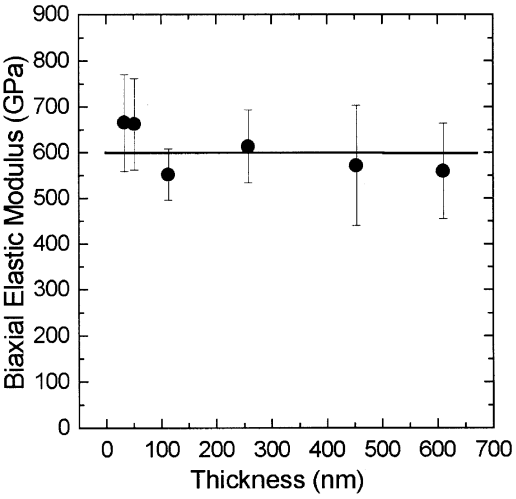


Fig. 6. Calculated biaxial elastic modulii of ta-C films for various film thicknesses.

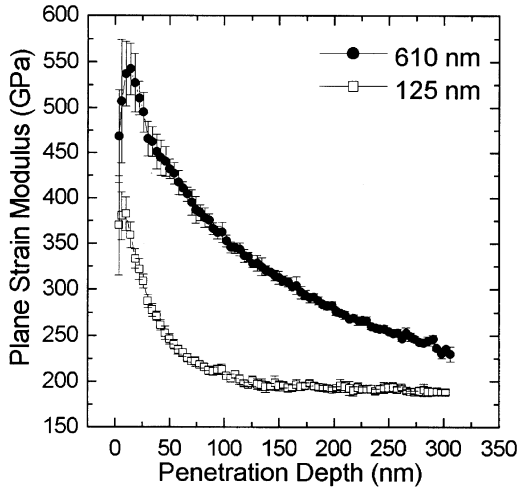


Fig. 7. Plane strain modulus of ta-C films of thickness 610 and 125 nm, respectively, measured by continuous stiffness measurement (CSM) mode of nanoindentation.

maximum value without a plateau, which implies that the mechanical properties of the substrate affects the measured value, even when the penetration depth of the indenter is significantly less than 10% of the film thickness. Furthermore, the maximum value for the 125 nm thick film is much lower than that in the 610 nm thick film, which is due to the more significant substrate effect in the former. This result shows that careful consideration of substrate effect is required when measuring the elastic modulus of thin films by nanoindentation.

4. Conclusions

We measured the biaxial elastic modulus of very thin DLC films of thickness down to 33 nm using the free overhang method. In contrast to other measuring methods, the free overhang method is not sensitive to the mechanical properties of the substrate because the substrate was removed to measure the strain of the film required to adhere onto the substrate. The method could be applied to measure the elastic properties of various DLC films from polymeric a-C:H film deposited by r.f.-PACVD, to the very hard ta-C film deposited by FVA process. In a-C:H film, the present work showed a decrease in the elastic modulus of a very thin film with decreasing film thickness. On the other hand, ta-C films displayed a constant elastic modulus regardless of film thickness. This contrasting behavior of the elastic modulus with film thickness is presumably due to differences in structural evolution during the initial stage of film growth. These results show that a mechanical property measured for a thick film cannot be always used for a very thin film. Possible applications of very thin films would, therefore, require investigation of the mechanical properties of the film and structural evolution during the initial stage of growth for the specific deposition method, involved.

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