DEPENDENCE OF RESIDUAL STRESS OF DIAMOND-LIKE CARBON FILMS ON PRECURSOR GASES AND PROCESS PARAMETERS OF RF PACVD

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ABSTRACT

Residual compressive stress of diamond-like carbon (DLC) films was measured by beam deflection method. DLC films were deposited on thin Si wafers using r.f. plasma decomposition of methane and benzene. Negative bias voltage of the cathode was varied from −100 to −800 V and deposition pressure from 3 to 100 mTorr. When using benzene as precursor gas, the residual stress monotonically increases as increasing $V_b/\sqrt{P}$. (Here, V_b is the negative bias voltage of cathode and P the deposition pressure.) In case of using methane, however, the residual stress has a maximum value at $V_b/\sqrt{P}$ between 70 and 100 V/mTorr$^{1/2}$. Because of the difference in molecular size between benzene and methane, the mean free path of ions in benzene discharge is 5 times shorter than that in methane discharge. The contrasting behavior of residual stress is discussed in terms of the difference in ion energies at the specimen surface due to the difference in mean free path. On the other hand, total hydrogen concentration decreases as increasing $V_b/\sqrt{P}$ in both cases. This result thus shows that the total hydrogen concentration cannot be a key to understand the behavior of residual stress.

INTRODUCTION

Diamond-like carbon (DLC) films, also called hydrogenated amorphous carbon films, have attracted considerable interests owing to their unique combination of properties. The unusual combination of high hardness, optical transparency, low coefficient of friction, chemical inertness, and high electrical resistivity has stimulated studies for various applications [1]. However, the applications are limited due to a problem of poor adhesion on some substrates such as steel. Even if DLC film can be used for lubrication and wear-resistance coating, their application for steel bearing is yet limited.

Residual stress of DLC film is one of major reasons for the poor adhesion. Typical DLC films have high residual compressive stresses of up to 10 GPa, which result in the delamination of the thick films from the substrates [2, 3, 4]. Even on Si where DLC film has good adhesion, the thick films tend to delaminate from the substrate to relieve their stresses [2]. Therefore, understanding the behavior and the origin of residual stress is one of prerequisites for the application of DLC coatings.

It has been well known that energetic particles play an important role in structure and properties of DLC films [5, 6]. Many investigations reported a strong dependence of the residual stress on the ion energy. With increasing ion energy, the residual stress shows a maximum value at an ion energy between 20 and 100 eV [7, 8, 9]. This behavior of residual stress is correlated with the structural change from polymer-like to diamond-like and further to graphite-like one with increasing ion energy [5, 7, 10]. The ion energy is hence the most important experimental variable to determine the residual stress of the film.

In r.f. plasma assisted chemical vapor deposition (r.f.-PACVD), typical mean free path of ion is shorter than the dimensions of reactor. While being accelerated by sheath potential, the ions will experience collisions with neutral species or other ions. Consequently, the ion energy on the specimen surface is dependent not only on the negative bias voltage of the cathode (approximately same as the sheath potential) but on the mean free path of the ion. Because the mean free path decreases with increasing the pressure [11], the negative bias voltage and the deposition pressure have been considered as the major experimental parameters in r.f.-PACVD [8, 10, 12, 13, 14, 15].

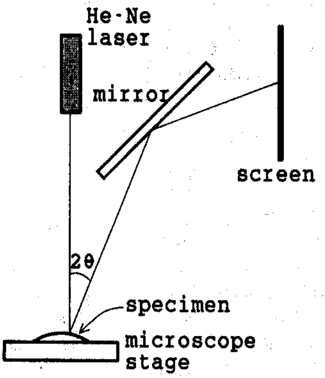

Figure 1: Schematics of the equipment for curvature measurement.

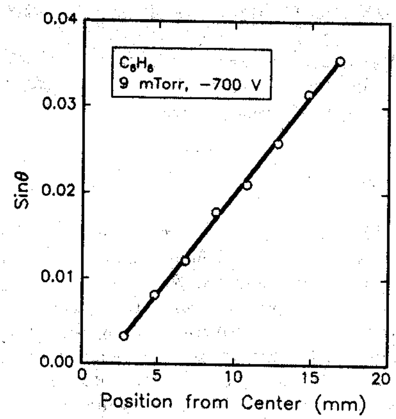

Figure 2: Measured Sinθ for various positions of specimen.

The size of molecules also affects the mean free path. (The mean free path is inversely proportional to the square of the diameter of molecule [11].) Hence, the ion energy at the specimen surface in r.f.–PACVD is also dependent on the precursor gases. Various hydrocarbon gases have been used for DLC film depositions. However, systematic observations of the precursor gas effect on the film properties have not yet been reported. In present work, the effect of the precursor gases on the residual stress of DLC film was investigated. The residual stresses were compared between films deposited from methane and benzene under the same value of negative bias voltage and deposition pressure.

EXPERIMENTAL METHOD

Film deposition

Diamond-like carbon films were deposited from r.f. plasma decomposition of methane or benzene. Details of the experimental set-up was previously described [3]. For the residual stress measurement, thin Si stripes of size 5mm × 50mm were cut from Si (100) wafer of 210±10 μm thick. Masked Si wafer of about 800 μm thick and Al foil were also used to measure the film thickness and the hydrogen concentration, respectively. The film thickness, the height of the step formed by the mask, was measured by an Alphastep profilometer. The total hydrogen concentration of the film was measured by combustion element analysis of carbon, hydrogen and nitrogen [16]. The error in the hydrogen concentration measurement is estimated to be less than 3 at.%. In order to improve adhesion of DLC films, the substrates were cleaned *in-situ* by an Ar discharge at −400 V and 3 mTorr for 15 min before deposition. Methane or benzene was then supplied at a fixed flow rate. The deposition pressure was controlled by adjusting the conductance of main valve. Deposition pressure ranges from 3 to 100 mTorr. Self bias voltage of the cathode was varied between −100 and −800 V by changing the r.f. power supplied. Depending on the negative bias voltage and the pressure, deposition was performed for 15 – 240 min.

Stress Measurement

All of deposited film–substrate composites were convex, showing that the residual stress is compressive. Fig. 1 shows an experimental set-up for the measurement of the curvature. The specimens were placed on a microscope stage that can move the specimen in precision of 0.1 mm. He-Ne laser beam was irradiated vertically down to the specimen surface. The direction of reflected beam is changed to a vertical screen by a mirror inclined by 45 degrees from the incident beam. The angles (2θ) between the incident and the reflected beam at various points on the specimen, were calculated from the heights of the reflected beam on the screen. Fig. 2 shows a typical curve of measured $sin\theta$ for various incident beam positions from the center of the specimen. The value of $sin\theta$ is linearly proportional to the distance, showing that the specimen is a part of circle. The curvature of the specimen is given by the slope.

The residual stress of the film was then calculated from the equilibrium equation of bending plates [17]:

$$\sigma = \frac{ED^2}{6rh(1-\nu)} \tag{1}$$

where σ is the stress in the film, D, E and ν are the thickness, elastic modulus and Poisson's ratio of the substrate, respectively, and r and h are the radius of curvature of the film-substrate composite and the thickness of the film respectively. A value of 1.8×10^2 GPa was used for $E/(1-\nu)$ of the Si (100) substrate [18]. Films with a minimum thickness of 0.5 μm were used for the measurement. The stress of the film is independent of the thickness in the range from 0.5 to 2 μm. The error in the stress measurement is estimated to be 10 – 15 %.

RESULTS AND DISCUSSION

The deposited films have high hardness, transparency and low coefficient of friction typical of DLC films. For example, the hardness ranges from 2000 to 4000 Kg/mm^2 in Knoop hardness scale, comparable to those of β-SiC or Al_2O_3. Deposition rate of the film is strongly dependent on the process parameters and precursor gases. Depending on the negative bias voltage, the deposition rate for benzene is 5 to 10 times higher than that for methane at the same deposition pressure.

For a precursor gas, the ion energy in r.f.–PACVD is known to be proportional to $V_b/\sqrt{P}$, where V_b is the negative bias voltage of cathode and P the deposition pressure [19]. The residual stresses of the films deposited from methane and benzene will be compared at the same value of $V_b/\sqrt{P}$. By taking this parameter as a common experimental variable, the only effect of precursor gases can be investigated. Hydrogen plays an important role in the structure and thus the properties of DLC films [5]. The dependence of hydrogen concentration will be also illustrated. Fig. 3 shows the measured residual stress and hydrogen concentration for methane and benzene.

Different behavior of residual stress was observed depending on the precursor gases. Residual stress of the film deposited from methane shows a maximum at $V_b/\sqrt{P}$ between 70 and 100 V/mTorr$^{1/2}$ as shown in Fig. 3 (a). This result is consistent with previous investigations on the effect of ion energy and the change of film structure [7, 8, 9, 10]. In the case of benzene, however, maximum of the residual stress does not occur in present experimental range (see Fig. 3 (b)). The residual stress continuously increases as the parameter $V_b/\sqrt{P}$ increases from 30 to 500 V/mTorr$^{1/2}$. This contrasting behavior will be discussed later.

On the other hand, the total hydrogen concentrations are inversely proportional to the parameter $V_b/\sqrt{P}$ in both cases of methane and benzene. In the range of $V_b/\sqrt{P}$ from 30 to 250, hydrogen concentration for benzene decreases from 32 to 22 at.%, and that for methane decreases 37 to 30 at.%. This result shows that the contribution of total hydrogen concentration is not a key to understand the behavior of residual stress. Nir also studied the effects of hydrogen partial pressure on the residual stress in Ar ion beam sputtering [20]. The residual stress changes only by 30 %, when the partial pressure of the hydrogen increased by more than a factor of 5. Furthermore, even when the hydrogen to carbon ratio arriving at the specimen surface was varied by 50 %, the stress ramained same [20]. His result also showed the negligible effect of hydrogen

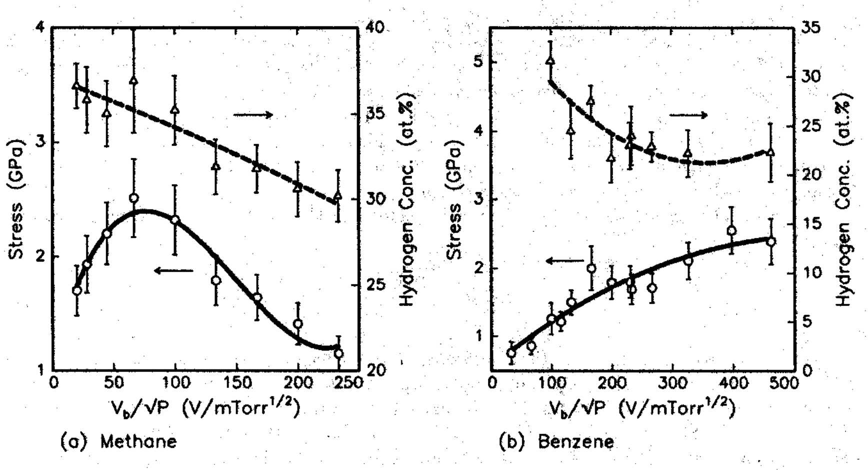

Figure 3: Dependences of residual stresses and hydrogen concentrations on $V_b/\sqrt{P}$ for (a) CH_4 and (b) C_6H_6.

concentration on the residual stress. However, the hydrogen in the film exists in both chemically bound and nonbonded states [21]. The roles of chemically bound and nonbonded hydrogen in the residual stress have not yet been clarified.

A possible explanation of the contrasting behavior of residual stress can be given by considering the difference in molecular size between methane and benzene. The diameters of the molecules can be estimated from the bond lengths of C–H bond in methane (1.091Å), C–C bond in aromatic compounds (1.395Å) and C–H bond in benzene (1.084Å) [22]. The diameter of benzene is about 2.3 times larger than that of methane. Furthermore, dominant ionic species in benzene discharge is $C_6H_6^+$, while methane discharge shows an abundance of CH_5^+ and $C_2H_5^+$ ions [23]. Hence, it can be assumed that the size of ion species is equal to that of neutral one in each case. Because the mean free path of molecule is inversely proportial to the square of the diameter, mean free path of ionic species in benzene discharge is about 5 times shorter. While being accelerated by the cathode sheath potential, an ion will experience about 5 times higher number of collisions in benzene discharge. (The difference in cathode sheath length between methane and benzene discharge is not significant.) Even at the same value of $V_b/\sqrt{P}$, therefore, the ion energy at the substrates in benzene discharge will be much smaller than that in methane discharge. As can be seen in Fig. 3, the residual stress for benzene shows a characteristic behavior of low energy deposition of methane. By simply assuming that the ion energy in benzene discharge is 5 times lower than that in methane discharge and the maximum residual stress appears at the same ion energy, the maximum residual stress for benzene will occur at $V_b/\sqrt{P}$ between 350 and 500 V/mTorr$^{1/2}$. This value is the upper limit of the present experimental range. More experimental work of higher negative bias voltage and lower deposition pressure is in progress.

The hardness of the film deposited from benzene also shows a characteristic behavior of lower ion energy deposition. In the range of $V_b/\sqrt{P}$ from 100 to 250 V/mTorr$^{1/2}$, the hardness of the film deposited from benzene increases from 2100 to 3400 Kg/mm^2, while that from methane decreases from 3600 to 2200 Kg/mm^2. Although the structure of the film are not investigated in present work, the structural change from polymer-like film to diamond-like one may occur in the films obtained from benzene in this range of $V_b/\sqrt{P}$.

CONCLUSIONS

The ion energy on the substrate in r.f.–PACVD is dependent not only on the sheath potential but on the mean free path of the ions. In addition to the deposition pressure, the molecular size of precursor gas should be thus considered for the ion energy estimation. The ion energy can be smaller in the discharge of larger molecules due to the reduction of the mean free path. Present experimental result agrees with this possibility. Even in the same range of sheath potential and deposition pressure, the residual stress and hardness of the film deposited from benzene show characteristic behaviors of lower energy deposition than that from methane. For direct evidence of this possibility, however, more elaborate plasma characterization is desirable.

Even if hydrogen plays an important role in the structure of DLC films, present work shows that the total hydrogen content in the film is not correlated with the residual stress. However, it must be noted that the hydrogens exist in several forms in the film [5]. In order to elucidate the role of hydrogen, the effect of the hydrogen in each state should be separated. An experimental work is in progress in order to quantitatively measure the hydrogen content in each state.

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