Deposition of High-Density Amorphous Carbon Films by Sputtering in Electron-Beam-Excited Plasma

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This study focuses on the deposition of high-density amorphous carbon films by sputtering enhanced by electron-beam-excited plasma. The energies and densities of argon ions and electrons in plasma were controlled by changing deposition conditions such as target-substrate distance, target bias voltage, operating pressure and discharge voltage to produce an electron beam. As a result, amorphous carbon films with different densities ranging from 1.7 to 3.1 g/cm³ were synthesized. X-ray photoelectron spectroscopic analysis indicated that the amount of sp³ carbon bonding was higher in the amorphous carbon film with a density of 3.1 g/cm³ than in that with a density of 1.7 g/cm³. Differences in surface profiles were not observed among amorphous carbon films with various densities; however, a friction test revealed that the frictional properties of amorphous carbon films depend on their densities.

1. Introduction

Amorphous carbon (a-C) film is an attractive coating material in terms of hardness, lubricity, and wear resistance. In addition, a-C film has a smoother surface than chemical vapor deposited (CVD) diamond films so that surface finishing is unnecessary for applications. Because of these properties, a-C film has been used for the surface treatment of cutting tools, molds, and hard disks. In order to realize further applications, improvement of film properties is required with regard to mechanical strength, surface flatness, and uniform thickness. Improving these characteristics will enable us to increase the number of the applications of a-C films, in particular for films several nanometers thick.

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Previously, researchers have reported that a-C films of higher densities contain higher sp³ hybridized carbon fractions,\(^{(1-3)}\) so it is expected that a-C films containing higher sp³ fractions have a higher mechanical strength and hardness. In fact, the hardness of a-C film tends to increase with the sp³ carbon fraction in a-C film.\(^{(4)}\) Thus, it should be possible to achieve superior mechanical properties in a-C film by increasing its density.

The densities of hydrogenated a-C films synthesized by chemical vapor deposition are reported to be in the range of 1.0~3.0 g/cm\(^3\), while 2.2~3.2 g/cm\(^3\) is typical for a-C films synthesized by physical vapor deposition (PVD).\(^{(3-5)}\) This grouping suggests that PVD is useful for producing high-density a-C films. However, PVD methods for depositing a-C films using vaporization and excitation of solid carbon sources have several drawbacks. One of the major disadvantages is the incorporation of microparticles, so-called droplets, into the films, which results in the degradation of surface smoothness and uniformity of thickness. Although droplet-free a-C films can be deposited using a filtered cathodic vacuum arc or a mass-separated ion beam, large-scale and sophisticated equipment is generally required. In contrast to these methods, it has been reported that enhancement of electron-beam-excited plasma during ion-beam sputtering prevents deposition of microparticles in/on a-C films;\(^{(6,7)}\) however, deposition conditions for synthesizing high-density a-C films having both a smooth surface and uniform thickness have not yet been fully investigated.

This study focuses on the deposition of high-density a-C films by sputtering enhanced with electron-beam-excited plasma. First, the deposition conditions that lead to the deposition of high-density a-C films were investigated, and second, the relationships between film density and the property along with the structure of films were examined.

2. Deposition Method and Estimation of Density

Figure 1 shows a schematic drawing of the electron-beam-excited plasma PVD system used for a-C film deposition. An electron beam source is installed on the bottom of the SUS304 chamber 70 mm in diameter. A graphite ring plate (purity 99.5\%), as a carbon

![Fig. 1. Schematic drawing of electron-beam-excited plasma.](image-url)
source, is placed 10 mm above the electron beam exit, and a substrate is set directly above the beam source at a certain distance. Both the graphite target and substrate are immersed in the plasma during deposition. The substrate holder is cooled by water so that the substrate temperature is maintained under 100°C. The distance between the substrate and the target varies with the longitudinal position of the substrate holder.

First, the graphite heater placed in the cylindrical LaB₆ cathode is heated to 1500°C in order to generate thermoelectrons. Second, a voltage is applied between the heated LaB₆ cathode and the copper anode surrounding the cathode to emit thermoelectrons. Finally, the thermoelectrons are directed out of the electron beam source by a magnetic field generated using a coil current and an electric field formed with the bias voltage. Argon plasma is generated by collisions between thermoelectrons and argon gas molecules supplied into the chamber. The electron beam current reaches 120 A because of the large cathode surface area of 50 cm². As a stable electron beam, the electron energy of which is around 100 eV, can be directed, argon atoms are effectively ionized and high-density plasma is generated at low pressures of approximately 10⁻² Pa. Amorphous carbon film is formed by carbon species that are generated by sputtering of the graphite target and deposit on the substrate after traveling through the argon plasma. The amount of sputtered carbon species depends on the bias voltage applied to the target.

The deposition conditions to synthesize high-density a-C films were optimized by changing the target-substrate distance, the target bias voltage, the pressure in the chamber and the discharge voltage between the cathode and the anode. Table 1 lists the deposition conditions. The deposition time is 2 h and the substrate is (100) silicon 2 inches in diameter. Pressure in the chamber is evacuated below 2×10⁻⁴ Pa prior to deposition to prevent contamination.

The density of a-C films was determined by the following procedures. A certain area of the substrate was masked before deposition. After deposition, several steps that were formed between the surfaces of the a-C film and the masked substrate were measured by atomic force microscopy (AFM) and the average of the measured values was regarded as the film thickness. Afterwards, the mass of a-C film was determined by measuring the difference in mass of the substrate before and after. It should be noted here that a wide deposition area about 1500 mm² resulted in an a-C film mass of 0.050–0.200 mg, compared with the substrate mass of about 2250 mg, which is believed to lead to small errors in the film mass measurement. The film thickness was confirmed to be uniform within ±5% over an area 2 inches in diameter in advance of the determination of the film density, which was calculated by dividing the mass of the film by its volume.

Table 1
Deposition conditions.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target bias voltage</td>
<td>0 ~ -350 V</td>
</tr>
<tr>
<td>Target-substrate distance</td>
<td>150~400 mm</td>
</tr>
<tr>
<td>Pressure</td>
<td>2×10⁻²–1.2×10⁻¹ Pa</td>
</tr>
<tr>
<td>Discharge voltage</td>
<td>40–120 V</td>
</tr>
<tr>
<td>Deposition time</td>
<td>2 h</td>
</tr>
<tr>
<td>Substrate</td>
<td>Si (100)</td>
</tr>
<tr>
<td>φ 50 mm t=500 μm</td>
<td></td>
</tr>
</tbody>
</table>
3. Relationship between Deposition Conditions and Film Density

3.1 Effect of bias voltage to target

In the deposition method employed, the properties and microstructure of a-C films depend on the state of the sputtered carbon species. Several conditions affect the state of the sputtered carbon species, one of which is the bias voltage applied to the graphite target because the number and energy of argon ions impinging on the target surface vary with the bias voltage. First, the optimum bias voltage was determined with respect to the growth of a-C films.

In the case of a bias voltage of 0 V, the substrate surface was etched at approximately 4 nm/h and deposition of a-C film was not observed. This etching is caused by argon ions in the plasma. As the bias voltage was decreased from 0 V, etching rates of the substrate were reduced while a-C films were deposited at bias voltages ranging from –150 to –350 V. In this case, argon plasma is generated in the wide region above the electron beam source as shown in Fig. 2(a). Deposition rates increased as the bias voltage decreased; however, droplets were formed in films at a bias voltage below –350 V. In addition, local discharge, which is identified with an arrow in Fig. 2(b), occurs at the edge of the target when the bias voltage is –350 V. Therefore, the bias voltage to the target was fixed at –300 V to synthesize a-C films at higher growth rates without droplets.

3.2 Effect of distance between target and substrate

The number and energy states of carbon particles that reach a substrate vary with the position of the substrate and affect the quality of a-C films. Hence, the distance between the target and the substrate was changed to 150, 280, and 400 mm. Figure 3 shows optical microphotographs of a-C film surfaces deposited at the three substrate positions. In the case of the distances of 150 and 280 mm, droplets and film delamination are observed as shown in Figs. 3(a) and 3(b). In contrast, smooth and topographically uniform film is deposited at a distance of 400 mm.

Raman spectroscopic analysis was carried out for the a-C films deposited at 150 and 400 mm and the results are shown in Fig. 4. The Raman shift of the a-C film at 150 mm shows a spectrum similar to that of microcrystalline graphite or glassy carbon, while the spectrum of the a-C film at 400 mm has a broad peak that is typical of tetrahedral a-C film. This
Fig. 3. Optical microphotographs of a-C films deposited at different distances from graphite target.

Fig. 4. Raman spectra of a-C films prepared at different distances between plasma source and substrate.
analysis suggests that a longer target-substrate distance corresponds to the formation of amorphous structures of carbon. Regardless of the distance between the target and substrate, the amount of carbon particles sputtered is constant if the target arrangement and the bias voltage applied to the target are the same. When the target-substrate distance is shorter, however, carbon species are not fully excited by collisions with active atoms, ions, and electrons in argon plasma after sputtering. As a result, many sputtered carbon species that consist of more than a single atom and have a low energy reach the substrate and form droplets as well as a-C films with low adhesion and a partially micro-graphitic structure. Consequently, a target-substrate distance of 400 mm was determined to obtain smooth amorphous films without droplets.

3.3 Effect of discharge voltage and pressure in chamber

The density of a-C film is closely connected to the hybridization state of carbon atoms in the film; the state of carbon species before deposition affects the microstructure of a-C films. Hence, the discharge voltage applied between the cathode and the anode and the pressure during deposition was varied from 40 to 100 V and from $2 \times 10^{-2}$ to $1.2 \times 10^{-1}$ Pa, respectively, to control the excitation of sputtered carbon species. The number and energy of argon ions in plasma vary with the beam current and energy of the electrons determined by the discharge voltage and the pressure. The relationship between the density of a-C films and the discharge voltage is shown in Fig. 5. Higher densities of a-C film are achieved at a discharge voltage of 60 V and an operating pressure of 5 or $10 \times 10^{-2}$ Pa. Figure 6 shows the relationship between the film density and operating pressure at a constant discharge voltage of 60 V. This figure suggests that a higher density film is obtained when the pressure is in the range from 5 to $10 \times 10^{-2}$ Pa, and consequently an optimum discharge voltage and operating pressure exist for synthesizing high-density a-C films.

![Fig. 5. Variation of film density as a function of discharge voltage.](image-url)
In order to discuss the growth mechanism of high-density a-C films, the ion current that is generated by the influx of argon ions to the target was measured under various combinations of discharge voltage and pressure. Figure 7 illustrates the variation of the ion current and shows that higher ion currents result with higher discharge voltages and higher pressures; the number of argon ions that reach the target increases at higher discharge voltages and pressures. Thus, a large amount of the graphite target is sputtered at higher discharge voltages and pressures so that excess carbon species are produced; the number of carbon species that are insufficiently excited in plasma increase and low-density a-C films are formed. On the other hand, the number of argon ions that reach the target decreases because the ion current between the target and the ground decreases as the discharge voltage and the pressure decrease. In this case, moderate amounts of carbon species were supplied; however, the number of active species in plasma decreases. Thus, sputtered carbon species are not activated fully in plasma and low-density a-C films are deposited.

4. Relationship between Film Density and Film Properties

4.1 XPS analysis

X-ray photoelectron spectroscopic (XPS) analysis was carried out on a-C films in order to evaluate sp² and sp³ bonding fraction ratios. Figure 8 shows XPS spectra of the a-C films with different densities. The spectrum of the high-density film is dominated by the peak due to the bonding energy (285.3 eV) of sp³ carbon and that of the low-density film by the peak due to the sp²-carbon bonding energy (284.5 eV). Estimation of the sp³ bonding ratio in both a-C films from the separation of the peak into sp²- and sp³-carbon bonding origins yielded 74% sp³-bonding fraction for high-density a-C film and 46% for low-density a-C film. Therefore, the sp³-carbon fraction in high-density a-C film is confirmed to be higher than that in low-density a-C film.
4.2 Surface profiles

The surface smoothness of a-C films was examined using an atomic force microscope, and the surface topographies are shown in Fig. 9. Both high- and low-density films have smooth surfaces over an area of 100 μm². The surface roughnesses of high- and low-density film are almost the same at 0.25 and 0.32 nmRa, respectively. Thus, it can be concluded that the surfaces of a-C films are smooth regardless of film density.

4.3 Tribological properties

Tribological properties are among the most important mechanical properties of coating materials, and they have been examined for a-C films of various densities. From previous
AFM observations, the effects of surface roughness on the tribological properties of a-C films with various densities are eliminated in the sliding tests.

The tribological performance of a-C films was evaluated using a ball-on-disk test apparatus. Table 2 lists the friction measurement conditions. Figures 10 and 11 show the relationship between friction coefficient and sliding distance and the observations of wear tracks formed on both silicon substrates and balls, respectively.

The low-density film (1.7 g/cm³) shows higher friction coefficients at the beginning of the sliding test. The coefficients ultimately reach the same values when a sliding test is carried out on an uncoated silicon substrate. This variation of friction coefficients is believed to occur because the a-C film is gradually removed as the distance increases according to the observation in Fig. 11(a) that shows the bare surface of the silicon substrate appearing after the sliding test. The friction coefficients would increase as the direct contact area between the steel ball and the silicon substrate grows. Finally the friction coefficient would
demonstrate almost the same values as it has under lubricant-free conditions. The highest density film (3.1 g/cm³) shows relatively high friction coefficients throughout the entire sliding test although the film is partially delaminated and its debris remains on the track as shown in Fig.11(c). In addition to high friction coefficients and debris, a large wear mark is observed on the surface of the ball. Although the high-density film is durable in terms of adhesion against the sliding test and most of the film remains, wear debris from the film may cause higher friction and large wear by working as abrasive particles. Concerning the a-C film with a slightly smaller density of 2.6 g/cm³, no delamination of the a-C film is shown in Fig. 11(b), implying superior wear resistance, which is considered to contribute to low friction. As a result, tribological properties of a-C films such as low friction and high wear resistance vary with film density and are optimized at a specific density.

5. Conclusions

Amorphous carbon films with various densities were synthesized by electron-beam-excited plasma PVD under controlled deposition conditions with respect to target-substrate distance, target bias voltage, operating pressure and discharge voltage for producing an
electron beam. Optimizing the deposition conditions resulted in the preparation of a-C film with a high density of 3.1 g/cm$^3$. XPS analysis indicated that the sp$^3$-carbon bonding fraction ratio in the a-C film with a density of 3.1 g/cm$^3$ was higher than that in the film with a density of 1.7 g/cm$^3$. The surfaces of a-C films measured by AFM were smooth regardless of the density, while ball-on-disk sliding tests revealed that the tribological properties such as friction and wear depended on the density. In particular, the a-C film with a density of 2.6 g/cm$^3$ showed low friction coefficients and high wear resistance.

References