Formation of a-C thin films by plasma-based ion implantation

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Abstract

Carbon films were prepared on a Si wafer substrate by using a plasma-based ion implantation (PBII) technique. The homogeneity of the carbon films formed on the three-dimensional object and the influence of the duty ratio of the pulse bias to the target on the property of the carbon films were investigated. The homogeneity of the carbon films formed on a convex face and that formed on a concave face by the incidence of the microwave to the target with a low angle of about $-30^\circ$ was almost a constant. The application of the ECR plasma source, with a mirror field, to the PBII system was efficient enough to improve the homogeneity, even though the plasma density was not very high. Diamond-like carbon films with a flat surface and a low friction coefficient can be formed by applying negative high-voltage pulses to a substrate with a low duty ratio of 1%. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Plasma-based ion implantation; ECR plasma with a mirror field; Carbon film; Chemical bonding; Mechanical properties

1. Introduction

Ion-beam-assisted deposition is an efficient technique for the synthesis of metastable hard materials, such as cubic boron nitride and diamond-like carbon (DLC), under low-temperature and low-pressure conditions [1–3]. These materials can be used on tools, engine gears, bearings, and so on. However, it is difficult to apply this technique to the surface modification of three-dimensional or complex-shaped objects because of the line-of-sight process of ion beams.

A new surface modification technique called ‘plasma-based ion’ (PBII), is currently being studied [4–6]. The PBII technique can modify surfaces of objects by applying negative high-voltage pulses to the object immersed in plasma. The PBII technique has excellent properties. It is easy to apply a three-dimensional or complex-shaped object; it is a simple component, and can obtain high-current density. Therefore, the PBII technique is expected to be cost effective. Recently, some fundamental studies have been conducted to apply the PBII technique to three-dimensional objects, such as a trench [7,8], sphere [8], and interior of a tube [9]. These studies show that the PBII technique is superior to conventional deposition systems that use ion beams to modify surfaces of the three-dimensional objects, due to the improvements in the thickness distribution of deposited or sputtered films. However, more homogeneity is required before more practical applications are made to such objects as engine gears, for example. The uniformity of properties, such as that exhibited in tribology, also has to be studied using this technique.

For the uniform modification of the surface of complex-shaped object, the problem to be solved is how to form the plasma sheath along the geometry of the surface of the object, for the uniform modification of the surface of complex shaped object. As the ions in the plasma are accelerated perpendicularly through the plasma sheath, it is necessary to decrease the width from the surface of the object to the edge of the plasma sheath for the formation of the plasma sheath along the surface of the object. The width of the plasma sheath decreases with increasing plasma density or decreasing pulse duration [10,11]. There are some plasma sources that make a high-density plasma, such as a helicon wave excited plasma [12], an inductively coupled plasma [13], and an electron cyclotron resonance (ECR) plasma. In these plasma sources, an ECR plasma can make a dense plasma with large volume [14], and a higher density plasma can be formed by making a mirror field to an ECR plasma source [15].

In this study, carbon films, which are expected to contain low-friction materials, were formed by using the PBII system with an ECR plasma source, with a mirror field.
The homogeneity of the carbon films formed on the three-dimensional objects and the influence of the duty ratio of the pulse bias to the target on the property of the carbon films, such as the chemical bond, the structure, and the tribological property, were investigated.

2. Experimental

A schematic diagram of a PBI system developed in this study is shown in Fig. 1. An ECR plasma with a mirror field was used to generate a high-density plasma. This system was composed of two electromagnetic coils with a maximum magnetic flux density of 200 mT, a microwave generator with an excitation frequency of 2.45 GHz at a maximum power of 2.8 kW and a wave guide. The mirror ratio, which is the intensity ratio of the magnetic flux density at the center of the electromagnetic coil and that at the center of the vacuum chamber, was 2. The ECR discharge point, which is 87.5 mT with an excitation frequency of 2.45 GHz, could be adjusted to any point along the horizontal axis in the vacuum chamber by changing the current of the electromagnetic coils.

The sample holder insulated from a vacuum chamber was connected to a high-voltage power supply with a pulse generator. The high-voltage pulse generator is able to supply voltage pulses up to $\pm 10$ kV and currents up to 20 A. A tube was used to switch the high-voltage pulses.

Si (100) wafers cut into 10 mm $\times$ 40 mm $\times$ 0.5 mm were used as substrate materials for the deposition of the carbon film. The substrates were placed on a water-cooled substrate holder made up of stainless steel. CH$_4$ gas was used as a raw material. The chamber was evacuated below $5.0 \times 10^{-4}$ Pa before deposition and carbon films were formed at a pressure of $4.8 \times 10^{-2}$ Pa. The input microwave power required to generate the plasma was 200 W. The current of the magnetic coils was 300 A and the ECR discharge point was set at about 100 mm from the center of the chamber.

For the investigation of the homogeneity of the carbon films formed on the three-dimensional objects, the substrates were placed on the surface of the concave or convex substrate holder. The relationship of the microwave-incident angle and the position of the substrate is shown in Fig. 2. The length of each side and the height of the convex- and the concave-shaped substrate holder were 10 and 80 mm, respectively. The microwave-incident angle to the target was changed from 0 to 180° for the convex faces. The incident angle of 0 and 180° means that the substrates were placed both in the front and in the rear of the microwave-incident direction. The microwave incident angle to the target for the concave faces was changed from 0 to $-90^\circ$. The $-90^\circ$ incident angle means that the surface of the substrate and the microwave-incident direction were parallel in the trench. The duty ratio of the pulse bias and the pulse voltage to the target were 1% and $-2$ kV, respectively.

For the investigation of the influence of the duty ratio of the pulse bias to the target for the property of the carbon films, the duty ratio of the pulse bias was changed from 0 to 50%, and the pulse voltage was $-2$ kV.

The thickness of the film was measured by the surface profilometer. Raman spectroscopy was used to characterize the structure of the films. The C–H stretch absorption of the films was measured by Fourier transform infrared (FT-IR) absorption spectroscopy. The hydrogen content of the film was measured by an elastic recoil detection analysis (ERDA). The surface morphology of the film was observed by atomic force microscopy (AFM). The tribological experiment was performed by ball-on-disk type friction test conducted with a 1N normal load in dry air at room temperature. The mating material was SiC ball with a diameter of 6 mm, and sliding speed was 20 mm s$^{-1}$.

3. Results and discussion

3.1. Homogeneity of the plasma

The electron density in the CH$_4$ plasma was measured by using a Langmuir single probe at the center of the vacuum chamber. The relationship between the electron density and the microwave power by changing the reaction pressure in the CH$_4$ plasma is shown in Fig. 3. The electron density was

![Fig. 2. The relationship of the microwave incident angle and the position of the substrate: (a) convex face, (b) concave face.](image-url)
increased by increasing the microwave power and the reaction pressure. The distribution of the electron density along the microwave-incident axis in the CH₄ plasma is shown in Fig. 4. The microwave power and the pressure were 200 W and 4.8 × 10⁻³ Pa, respectively. The electron density was almost a constant, ~3 × 10¹⁰ cm⁻³ of length 190 mm. This shows that the ECR plasma source with a mirror field can form uniform plasma widely, which is efficient for the PBII treatment.

A distribution of the thickness of carbon films formed with or without the application of pulse bias placed on each surface of the convex and concave substrate holder against the microwave-incident angle is shown in Fig. 5. The film thickness formed on a convex face and that formed on a concave face by the incidence of the microwave to the target at a low angle within −30° was almost a constant. The thickness of the films formed on a concave face by the incidence of the microwave to the target at an angle of less than −45° was decreased by decreasing the microwave-incident angle. This result estimates that the plasma density around the convex face was uniform, as that of the concave surface was decreased in this plasma generating condition. The distribution of the film thickness formed with or without the application of pulse bias showed almost the same tendency, because radicals and ions which contribute to form carbon films with or without the application of pulse bias were supplied from the plasma around the surface of the substrate. However, the uniformity of the film thickness was improved considerably compared to the conventional deposition technique using an ion beam, which cannot modify the rear side of the substrate against the ion source. It is assumed that the application of the ECR plasma source with a mirror field, which can form the uniform plasma in wide space, to the PBII system was efficient enough to improve the homogeneity of the thickness of the films, even though the electron density was not very high at 3 × 10¹⁰ cm⁻³. It is also assumed that the homogeneity to the concave face will be improved when the plasma density is increased as the ECR plasma source is used with a mirror field.

3.2. Influence of the duty ratio on the property of the carbon films

The Raman spectra of the carbon films prepared by changing the duty ratio of the pulse bias to the target are shown in Fig. 6. The Raman spectra changed considerably with or without the application of the pulse bias to the substrate. When the pulse bias was not applied to the substrate, the Raman spectrum did not have a specific peak, and the background intensity was high. This shows that the film formed without the application of the pulse bias was a polymer-like
carbon film, which is composed of small ring sizes of aromatic molecules or polyene chains [16]. On the other hand, the Raman spectrum had a main peak at 1520 cm⁻¹ corresponding to the G-band and a shoulder peak at 1350 cm⁻¹ corresponding to the D-band [17], which showed the formation of DLC by the application of the pulse bias to the target. It shows that the structure of the film had changed considerably with or without the application of the pulse bias to the substrate. It is assumed that the polymer-like carbon film that had been deposited when no pulse bias had been applied was modified by irradiating the pulsed ion beam. The film structure can be changed by the irradiation of the ion beam with a low duty ratio of 1%. The intensity ratio of the D- and the G-band (I_D/I_G) increased when the duty ratio of the pulse bias to the target was increased and the peak position of the G-band was shifted for a higher wave number. It is assumed that the crystallite size in the film decreased when the duty ratio of the pulse bias was increased [3,17], and the structure of the film was changed from DLC to a structure that was similar to the glassy carbon that had a low density because of too much irradiation of ions.

The IR spectra of the carbon films prepared by changing the duty ratio of the pulse bias to the target are shown in Fig. 7. The broad absorption band centered at 2950 cm⁻¹ corresponding to the sp²-C–H bond and sp²-C–H bond [18] was observed in the film deposited without the application of a pulse bias. It shows that the polymer-like carbon film was formed without the application of the pulse bias to the substrate [18,19] and this result shows a good agreement with the result of the Raman spectra. On the other hand, this absorption band disappeared when the pulse bias was applied to the substrate. This means that the C–H bonds in the polymer-like carbon film were cut-off by the irradiation of the ion beam. It is assumed that the structural change observed by Raman spectra occurred by the reduction of the C–H bonds in the film with the irradiation of the pulsed ion beam.

The depth profiles of the compositions of the films deposited by changing the duty ratio of the pulse to the substrate obtained by ERDA are shown in Fig. 8. The interface between the film and the substrate was very clear in the film deposited without the application of the pulse bias. The mixing layer between the film and the substrate was formed by the application of the pulse bias. The thickness of the mixing layer increased when the duty ratio of the pulse bias to the target was increased. The increase of the duty ratio of the pulse bias causes an increase in the ratio of the irradiated ions and the film thickness deposited when no pulse bias was applied. It is assumed that the thickness of the mixing layer increased because the ions irradiated to the interface between the film and the substrate increased when the duty ratio increased. The relationship of the duty ratio of the pulse bias to the target and the hydrogen content in the carbon films is shown in Fig. 9. The content of the hydrogen in the film decreased with the application of the pulse bias, which was constant in spite of the changing duty ratio of the pulse bias to the target. However, more than 20% of hydrogen remained in spite of the irradiation of the ion beam. It is assumed that the hydrogen atoms in the carbon films were not bonded with carbon atoms and they existed in the interstitial site in the film as a result of the IR spectra, which showed a reduction of the C–H bonds in the film as a result of the application of the pulse bias.

The surface morphologies of the films obtained by changing the duty ratio of the pulse bias to the target observed by AFM are shown in Fig. 10. The surface was very flat by the application of the pulse bias with a low duty ratio of 1%. Blisters were formed as a result of the application of the pulse bias with a duty ratio of more than 10%, and the number of blisters increased when the duty ratio of the pulse bias to the target was increased. It is assumed that these blisters formed as bubbles that were filled up with
hydrogen by the irradiation of too many ions in the film. The relationship between the duty ratio of the pulse bias to the target and the mean surface roughness, \(R_a\), is shown in Fig. 11. The mean surface roughness increased when the duty ratio of the pulse bias to the target increased. This means that the irradiation of ions of a low duty ratio, such as 1\%, for example, is effective to form a flat surface.

The friction coefficients of the prepared films are shown in Fig. 12. The film that formed without the application of the pulse bias was peeled-off as soon as the friction test started, and the friction coefficient was 0.6, which is equal to that against the Si substrate. The friction coefficient was decreased to 0.1 by applying the pulse bias with a duty ratio of 1%. The friction coefficient increased to 0.2 when the duty ratio was increased. From the result of the Raman measurement shown in Fig. 6, the structure of the carbon film changed from DLC to one similar to glassy carbon with an increase of the duty ratio of the pulse bias. It is assumed that this structural change caused an increase in the friction coefficient. The tribological property of the carbon film can be improved by the application of the pulse bias with a low duty ratio in the range of 1%.

4. Conclusions

Carbon films were prepared on a Si wafer substrates by using a PBI technique. The homogeneity of the carbon films formed on the three-dimensional objects and the influence of the duty ratio of the pulse bias to the target on the property of the carbon films were investigated.

1. The homogeneity of the carbon films formed on a convex face and that formed on a concave face by the incidence of the microwave to the target at a low angle within \(-30^\circ\) was almost constant. It is assumed that the application of the ECR plasma source with a mirror field to the PBI system was efficient enough to improve the homogeneity of the property, even though the plasma density was not very high. It is also assumed that the homogeneity of the property to the concave face could be improved by increasing the plasma density by using the ECR plasma source with a mirror field.

2. DLC films with a flat surface and a low friction coefficient could be formed by the application of negative high-voltage pulses to the substrate with a low duty ratio of 1%. When the duty ratio of the pulse bias to the target was increased, the structure of the carbon film changed from DLC to a structure similar to the glassy carbon because the irradiation of ions had been excessive. The mean surface roughness and the friction coefficient of the carbon films increased when the applied duty ratio of the pulse bias to the target had been increased.
Fig. 10. The surface morphologies of the prepared films obtained by changing the duty ratio of the pulse bias to the target observed by AFM. (a) Duty ratio: 1%; (b) duty ratio: 10%; (c) duty ratio: 30%; (d) duty ratio: 50%.

Fig. 11. The relationship of the duty ratio of the pulse bias to the target and the mean surface roughness of the carbon films.

Fig. 12. The friction coefficients of the prepared films by changing the duty ratio of the pulse bias to the target.
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