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主　論　文　の　要　旨

論文題目　Study on high-speed plasma-enhanced chemical vapor deposition of conductive carbon by microwave power
(マイクロ波電力を用いたプラズマ気相成長法による導電性炭素膜の高速堆積に関する研究)

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論　文　内　容　の　要　旨

High conductive carbon has attractive material due to its superior characteristics such as high thermal conductivity, high electrical conductivity, anti-corrosion properties, and so on. For deposition of high conductive carbon film, some methods have been proposed such as chemical vapor deposition (CVD) with high temperature, physical vapor deposition (PVD), plasma-enhanced chemical vapor deposition (PECVD). However, these film deposition processes have issues such as low deposition rate, difficulty in enhancing the electrical conductivity, or uniform film deposition in large area. For example, typical deposition rate of high conductive carbon film is less than 1 nm/s in all processes mentioned above. These issues make commercialization of the graphite films difficult.

In this study, I propose new PECVD methods for the high conductive carbon film deposition using microwave plasma with high bias voltage (<2 kV), where high deposition rate is expected by high-density plasma. High electric conductivity is expected by increasing ion bombardment. Film deposition characteristics such as deposition rate, thickness uniformity, electrical conductivity, and film structure are studied. As a result, the carbon film is deposited with high electrical conductivity and high deposition rate ~5, 6 times higher than previous studies.

Present dissertation is composed of five chapters.

In Chapter 1, background and purpose were introduced. In the past 20 years, interest in the carbon coatings has increased significantly and studies for applying carbon coating to a lot of industrial fields have been carried out due to attractive features of carbon films, *i.e.*, chemical stability and high thermal conductivity. Furthermore, electrical conductivity, strength, and friction coefficient have been controlled by the sp^2 and sp^3 content ratio of the carbon film. Due to much studies of carbon film coating, the recent carbon films were deposited in well-defined conditions and could be selectively applied to various fields with required features. High electrically-conductive carbon film, which is amorphous carbon (a-C) or hydrogenated amorphous carbon (a-C:H) with a high sp^2 content ratio, is applied in electrodes, batteries, bearing and so on because of its high electrical conductivity and low frictional force. There are two typical methods for increasing the sp^2 content in the carbon film: heating the substrate over 500 ℃ or incident ion to the carbon film. However, heating the substrate has a problem in that the substrate may receive thermal damage. On the other hand, the ion bombardment effect can increase sp^2 even at lower temperatures. In the deposition methods of high conductive carbon film, there are 3 typical methods, *i.e.*, PVD, CVD, and PECVD. However, in the production of the high conductive carbon film, the low deposition rate less than 1 nm/s is a big problem.

To solve the above issues, three approach were adopted in this study. Firstly, microwave plasma, a high-density plasma source which can realize uniform plasma process in large area, was used. This plasma source contributes to enhanced productivity both from the viewpoint of high throughput with large-surface area and from the viewpoint of high process speed. Secondly, the high negative bias voltage was applied in this study. To increase the ion incident energy, high negative bias voltage up to -2kV was introduced for the ion energy enhancement. Finally, benzene gas was adopted as precursor gas because it has high deposition rate by its low ionization potential.

In Chapter 2, high-density microwave plasma sources used in Chapters 3 and 4, *i.e.*, surface-wave plasma (SWP) and electron cyclotron resonance (ECR) plasma, were explained. Both plasma sources have high plasma density over 1×10^{17} m^{-3}. The principles of both plasma sources were explained. Furthermore, to investigate plasma parameters, *i.e.*, plasma density, floating voltage, plasma voltage and electron temperature, Langmuir probe with its measurement principle was introduced. In addition, film evaluation methods, *i.e.*, a four-terminal sensing for the electrical conductivity measurement, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning and transmittance electron microscopy (STEM) and electron energy-loss spectroscopy (EELS) for the carbon film structure measurement, were explained. Fourier transform infra-red spectroscopy (FTIR) was also introduced for the evaluation of C-H bonds.

In Chapter 3, a high conductive carbon film was deposited by introducing SWP plasma. Firstly, plasma density spatial distribution is evaluated by Langmuir probe under Ar plasma. The plasma density decreased by increasing distance from quartz surface where the plasma density was the highest. At least the plasma density was distributed from 1×10^{17} m^{-3} to 8×10^{17} m^{-3}. The plasma density along with the width of the stage surface was uniform with high plasma density $\approx4\times10^{17}$ m^{-3}. Carbon films were deposited by changing bias voltage from 0.5 to 2.0 kV. The ion incident energy was related with the bias voltage. It means that the carbon films are deposited by different ion incident energy. The features of the carbon film were evaluated using measurement methods introduced in Chapter 2. The properties of the carbon film changed with increasing the ion incident energy. At high bias voltages, high conductive carbon films were successfully deposition. In parallel with the conductivity measurement, influence of the ion incident energy on the carbon film characteristics and structure were studied in detail. By increasing ion incident energy, the electrical conductivity of the carbon film increased and the deposition rate decreased. The reasons for the decrease in the deposition rate was explained by the change in the film structure and the sputtering effect. With increasing the ion incident energy, the hydrogen content in the film decreased and the sp^2 content ratio increased. When -2.0 kV was applied to the stage, the deposition rate was $\approx$6 nm/s, the hydrogen content evaluated by FTIR was less than 5%, and the sp^2 content evaluated by XPS was more than 70%. The carbon film was confirmed to be amorphous structure with nano-sized sp^2 clusters by STEM and EELS.

In Chapter 4, the high conductive carbon film was deposited by ECR plasma source. Higher plasma density ($\geq 1\times10^{18}$ m^{-3}) more than that of SWP was realized, especially when the bias voltage was applied to stage. The phenomenon of the plasma-density increase by the bias application was confirmed by OES and Langmuir probe. The increase in the plasma density was prominent when the low permeability material was used as the stage material, but not in the case of the high permeability stage. This suggested that the plasma increase was affected by the magnetic field near the stage. The reason for the plasma density increase was attributed to the secondary electrons those were generated by ion collision on the stage surface. They were accelerated by the sheath and were confined between the stage and the antenna due to the magnetic mirror effect and the sheath electric field, contributing to the effective ionization of the plasma. The confinement of the electrons was simulated by a charged-particle-trajectory simulator with collisionless condition. To explain the increase of plasma density, a theoretical zero-dimensional model of the plasma density was proposed. The plasma density increased and resultant increase of the ion flux to the stage affected the properties of the carbon film. The high conductive carbon film was deposited at bias voltages of $\approx$-1 kV which was lower than the case of the SWP in Chapter 3.

In Chapter 5, summary and future scope of this dissertation was introduced. The target purpose, *i.e.*, increase in the carbon film deposition rate was achieved as 5 to 6 times higher than that of previous works. The three approach points to increase the deposition rate of the conductive carbon film were effective. In addition, the effect of ion incident energy and ion flux to the carbon film properties and structure was mainly evaluated. To deposit the high conductive carbon film, either the high ion incident energy or the high ion flux was required. In the future scope, expected difficulty to apply industrial and the method to increase deposition rate more were discussed.