Effect of Spiral Microwave Antenna Configuration on the Production of Nano-crystalline Film by Chemical Sputtering in ECR Plasma

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Nano-diamond thin film has been successfully prepared by placing a Si substrate in front of a carbon target in pure hydrogen electron cyclotron resonance plasma. A quadrupole mass analyzer coupled to an orifice monitored the molecular species distributions produced at the surface of the carbon target. The measured mass distribution of the gas had clearly indicated that the observed hydrocarbon emission was due to chemical sputtering of hydrocarbon. The position of the microwave antenna as well as the electrical bias affected the molecular species from the carbon target, and these parameters can be utilized as the tuning knobs to control the film deposition condition.

Key words: Electron Cyclotron Resonance (ECR) Microwave Plasma, Chemical Sputtering, Nanocrystalline Film, Carbon, Hydrocarbon radical

1. Introduction

Diamond and diamond-like carbon films have been extensively studied due to its advantageous properties such as high mechanical hardness, chemical inertness, optical transparency, and high electrical resistivity. Various chemical and physical vapour methods have been successfully applied to prepare carbon films, such as plasma enhanced chemical vapour deposition (PECVD), ion beam assisted deposition (IBAD), pulsed laser deposition (PLD), cathodic arc deposition, and sputtering have been successfully utilized. 1-3)

Sputtering technique has been widely used due to its controllability of deposition conditions by adjusting plasma power and gas pressure that are nearly independent of substrate properties. Compared to dc and rf sputtering, higher sputtering yield of graphite can be achieved by electron cyclotron resonance (ECR) condition that increases the electron mean free path, hence, the degree of ionization of the plasma. 4) Based on this principle, a device that produces ECR plasma with a spiral microwave antenna coupled to a ring-shaped graphite sputtering target in a dc magnetic field has been designed and being tested.

The microwave antenna excites plasma locally making the antenna structure and distance between the antenna position and the graphite sputtering target important parameters that can affect system’s overall film deposition efficiency. Therefore, the device has been operated with different configurations to change the distance between the graphite target and the spiral antenna. The resulting flux of hydrocarbon and that of atomic hydrogen were compared by optical emission spectroscopy and mass spectral analysis. Morphology and crystal structures of produced nano-crystalline films were characterized by scanning electron microscopy and X-ray diffraction, respectively.

2. Experimental methods

2.1 Experimental device

Schematic diagram of the experimental system used in the study is shown in Fig. 1. It has a vacuum chamber of 340 mm in diameter and 230 mm in depth. A ring-shaped gas injection unit of 50 mm outer diameter and 38 mm inner diameter with 1 mm thick solid carbon
disk placed on its nozzles serves as a carbon radical source. Through chemical sputtering process, the unit supplies hydrocarbon molecules homogeneously to the deposition substrate.

The installed electromagnet generates a magnetic flux density of about 875 G at 50 mm above the carbon disk. The 2.45 GHz microwave supplied through a coaxial cable induces a high frequency electrical current to a spirally wound antenna made of nickel. Tested antenna configurations are: Far, Mid and Near, of distances 105 mm, 65 mm and 25 mm from the carbon sputtering target, respectively. The other end of the antenna is grounded.

2.2 Film preparation

The deposition target is heated up to 700 °C by an infrared radiation from a high temperature tungsten wire wound at the back of the deposition. Nano-crystalline films have been deposited on Si (111) of dimension 20 mm x 10 mm x 1 mm at 100 W microwave power for three hours at 10 Pa working pressure. The carbon sputtering target and the silicon substrate were biased at -400 V and 70 V against the chamber wall, respectively.

2.3 Hydrocarbon emission from carbon target

To monitor the particle flux near the surface of the carbon target, a quadrupole mass analyzer (SRS Co. Residual Gas Analyzer 200) was attached to an 18-mm diameter probe with 0.5-mm aperture facing the graphite disk along its vertical axis. The QMA ionizer located at the end of the tube system is about 22 mm from the aperture line-of-sight. The system is shown schematically in Fig. 2.

Light emission from the plasma was detected through a view port that observes the plasma region right beneath the gas injection unit. The light is transported by an imaging optical fiber attached to an Ocean Optics USB4000 spectrometer with 0.2 nm spectral resolution.

Fig. 1. Schematic diagram of the ECR-PECVD plasma device. The figure inset shows the position of microwave antenna with respect to the carbon target in each configuration.

Fig. 2. Schematic diagram of an orifice coupled to a quadrupole mass analyzer for the analysis of particle flux near the surface of the carbon disk target.
3. Results and discussion

3.1 Film morphology

Morphologies of the films produced using different microwave antenna configurations are shown in Fig. 3. Diamond structure of the films prepared with the far and mid configurations have been confirmed with X-ray diffraction, while no carbon peak has been detected for films prepared with near antenna configuration.

![Scanning electron micrographs of films deposited using (a) Near (b) Mid and (c) Far antenna configurations.](image)

Fewer grains are found at the near-antenna-formed film. On the other hand, it can be observed that larger and denser grains are found on a film produced using the far-antenna configuration. In the near antenna configuration, the deposition substrate was immersed in the plasma, and the ion sputtering of the produced film should hinder a stable formation of the film. For the far and mid antenna configurations, the formation rate of the film and the grain size distribution of the produced film are attributed to the production rate and species composition of flux of hydrocarbon at different microwave antenna positions.

3.2 Hydrocarbon emission

The effect of microwave antenna position on hydrocarbon production can be observed in Fig. 4 which displays the CH/H\textsubscript{α} intensity ratio evaluated from the optical spectrum of the plasma at varying H\textsubscript{2} working pressure. More hydrocarbon radicals were produced when the antenna was positioned closer to the graphite target. The shorter distance between the graphite target and the antenna increases incident ion energy making higher bond breaking probability. The decreasing trend as the pressure was raised can be accounted to the increased collisions with atoms not taking part in the bond breaking, which extract even more energy from the impinging particle. 5)

![Influence of pressure and antenna configuration on the intensity ratio of CH (387 nm) line and H\textsubscript{α} (656.3 nm) line.](image)

Shown in Fig. 5 is the superposition of mass spectra before and during ECR microwave plasma operation at 1 Pa H\textsubscript{2} pressure using the far-antenna configuration. The mass spectra revealed the increase in the hydrocarbon (CH) radicals during the plasma discharge.
Fig. 5. Mass spectra before and during ECR microwave plasma discharge using the far-antenna configuration.

The effect of microwave antenna position on hydrocarbon production can be observed in the mass spectra shown in Fig. 6. More carbon atoms were produced when the antenna was positioned closer to the graphite target, whereas more CHₜ radicals are generated when plasma was excited farther from the sputtering target.

To further investigate the factors affecting the CH production, mass spectrum signal intensities of carbon and hydrocarbon radicals were measured as functions of the electrical bias induced onto the carbon target. In Fig. 7, the increasing trend of C⁺ until saturation can be observed as the negative bias voltage was raised. At lower negative bias, CH₃⁺ and C₂H₃⁺ were formed together with almost equal amounts. As the sputtering target bias was increased, formation of C₂H₃⁺ decreases.

Fig. 6. Mass spectra of plasma excited using the far and mid antenna configurations.
Fig. 7. Partial pressure of carbon and hydrocarbon radicals as a function of the bias voltage induced on the graphite sputtering target. The plasma was excited using the far-antenna configuration.

The carbon hydride emission due to chemical sputtering of the graphite target by hydrogen plasma was confirmed through the observed increase in CH radicals in Fig. 5. Dense and large grains in the far-antenna-formed film are possibly due to the high CHx fluxes necessary for film growth as seen in Fig. 6. This event can result in a much higher plasma particles flux to the silicon substrate at near-antenna configuration, but ion flux that should be present in the configuration can cause erosion of the deposited film.

In the utilization of mid antenna, more C⁺ were observed due to the higher sputtering rate of carbon which in this configuration is closer to the antenna. As for the case of the far-antenna, it excited the plasma farther from the graphite target giving more room for carbon radicals to react with H⁺ thus enhanced the formation of CHx radicals.

Increased concentration of C₂H₃⁺ at lower bias voltage can be attributed to the high hydrogen adsorption on the surface of the target enhancing chemical sputtering. During that phase, the graphite target can be exposed to thermal atomic hydrogen producing the radicals C₃H₆ represented by C₂H₅⁺. The higher bias voltage corresponds to the increased energy of bombarding hydrogen, and the sputtering yield should be higher at higher bias, provided the same amount of hydrogen atoms are adsorbed. The decrease in C₂H₃⁺ partial pressure as the bias voltage was raised can be caused by depletion of hydrogen atoms near the surface of the carbon target leading to reduction of chemical sputtering.

4. Conclusion

A nano-diamond film was formed on a substrate by arranging a carbon target in ECR excited hydrogen plasma without supplying any hydrocarbon molecule. The particle flux from the carbon target during plasma operation was monitored with a quadrupole mass analyzer, and the result had clearly indicated the presence of both physical and chemical sputtering. The antenna configuration coupled to the target condition for optimizing the hydrocarbon emission can be further optimized based upon fundamental principles of chemical sputtering studied in plasma-wall interaction for fusion experiment devices.

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References


