Actinometry Measurements of Density Distributions of C\textsubscript{3} Radical and Hydrogen Atom in Thermal Plasma Chemical Vapor Deposition of Diamond

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Abstract

For the thermal plasma chemical vapor deposition (TPCVD) of diamond by the arc-jet thermal plasma, radial density distributions of major reactive species, such as hydrogen atom and C\textsubscript{3} radical generated in proportion to the methyl radical concentration, are measured near the substrate surface by the actinometry, for which the reactant gases are injected into the plasma jet by the two different methods: near-injection and far-injection. As a result of actinometry measurements for a case of the near-injection method, radial density distributions of both hydrogen atom and C\textsubscript{3} radical have the off-axis peaked profiles, which indicate low density in the central region and high density in the peripheral region of the plasma jet flame. These results may be explained from the fact that a high-velocity stream of the arc jet inhibits the injected reactant gases from penetrating effectively into the plasma flame center. On the other hand, the far-injection method shows somewhat uniform density distributions over the central region of plasma flame due to reasonable mixing effects of reactant gases. These measured results of actinometry are affirmatively supported by the Raman spectroscopy analysis of diamond thin films. Therefore, the far-injection method is expected to be preferable for getting the higher uniformity in the diamond thin film deposition.
1. Introduction

Among the diamond chemical vapor deposition (CVD) methods, the arc-jet thermal plasma CVD has very high deposition rates compared with the others, such as hot filament CVD or microwave plasma CVD. Thus, the arc-jet thermal plasma CVD is considered to be more suitable production process of diamond thin films for the industrial applications. However, the inherent steep temperature gradient of the arc-jet thermal plasma flame impedes the uniformly-distributed dissociations of reactant gases like hydrogen and methane for diamond CVD. Therefore, the uniformity of deposited diamond film has been reported to be somewhat lower in thermal plasma CVD compared with that of hot filament or microwave plasma one. For improving the uniformity of films deposited on the substrate, it is essential to know the information on radial density distributions of major reactive species, such as methyl radical and hydrogen, near the substrate surface.

The actinometry measurement is employed in this experimental work for investigating the radial density distributions of hydrogen atom and C2 radical generated in proportion to the methyl radical concentration in the arc-jet plasma diamond CVD. To improve the density uniformity of major reactive species in the plasma flame, the two gas injection methods are taken into account according to the distance from the anode nozzle exit, i.e., the near-injection and far-injection methods are investigated, respectively, in this research based on the actinometry measurement. In addition, the constituents of the diamond thin film deposited on the substrate are analyzed by means of the Raman spectroscopy, and their results are compared with the outcomes of measured density distributions of radical species. In the following, the experimental procedure is briefly introduced, and the measured results and discussions are presented.

2. Experimental Procedure

In this TPCVD experiment, a non-transferred dc arc-jet plasma torch is used to produce a thermal plasma, and argon is used as a plasma forming gas. The reactant gases of methane and hydrogen are injected into the plasma jet by the two different methods of near injection and far injection, respectively. In the near-injection method, an injection of methane and hydrogen is performed into the argon plasma flame at 2 mm just below the anode nozzle exit of the torch in order to maintain the arc more
stable and reduce the erosion of electrodes due to the pure inert plasma instead of the reactive hydrogen-mixed plasma. The far-injection method uses a methane injection into the premixed argon-hydrogen plasma flame at 7.0 cm far below the anode nozzle exit in order to increase mixing effects among reactant and plasma gases.

The actinometry measurement is a diagnostic method to measure the density distribution of radical by analyzing optical emission spectra from plasma flame. Because the optical emission line intensity is correlated with both of density and temperature, it is impossible to get density distributions of radicals from only one spectral intensity profile. Thus, the inert actinometer, of which the amount is small enough not to disturb the state of plasma, is added into the plasma flame. The density distributions of radicals can be acquired from a ratio of the emission line intensity of radical to that of the inert actinometer added without considering temperature effects on the emission line intensity. In the present experiment, the background emission of argon can be used as an actinometer emission without any additive inert gas because the argon is used as a plasma forming gas for the arc-jet thermal plasma.

An emission spectroscopy system, consisting of an optical fiber, a guide tube and its control unit, a monochromator system, is used for actinometry measurements of reactive species density for both injection methods. The emission line intensities from a tail region of the jet flame at 2.5 cm above the substrate surface are detected radially at intervals of 2 mm from the arc-jet plasma flame axis to its periphery where the emission line is indistinguishable from the background light. Emission spectral lines of 6965 Å for Ar, 6563 Å for H, 5165 Å for C₃ are selected for the measurements.

Diamond films have been deposited on the Mo substrate for a duration of 30 minutes with the following operation conditions: substrate temperature of 870 - 970°C, argon flow rate of 25 - 35 l/min, hydrogen flow rate of 5 - 10 l/min, methane flow rate of 0.5 - 1.0 l/min, ambient pressure of 60 - 160 Torr, input current of 250 - 400 A. The deposited films are analyzed by means of the Raman spectroscopy to identify their constituents and compare with the measured results of actinometry.

3. Results and Discussions

Fig. 1 shows radial distributions of H atom and C₃ radical measured at 7.5 cm from the nozzle exit of the torch operated with two input currents in the case of the
Fig. 1 (a) H density distributions and (b) intensity ratio distributions of C2 peak to Ar peak for a case of near-injection method, where arc input currents are measured at 7.5 cm from the nozzle exit with Ar 25 l/min, H2 10 l/min, CH4 1.0 l/min and 60 Torr.

Fig. 2 Relative intensities obtained from Raman spectroscopy (a) at a center region and (b) at a peripheral region of the diamond film deposited for 30 minutes in a case of near-injection method with input current 300 A, Ar 25 l/min, H2 10 l/min, CH4 1.0 l/min and 60 Torr.
near-injection method in the following operation conditions: Ar flow rate of 25 l/min, H₂ flow rate of 10 l/min, CH₄ flow rate of 1.0 l/min and ambient pressure of 60 Torr. The radial distributions of the hydrogen atom density and the ratio of C₂ intensity peak to Ar have the off-axis peaked profiles for all the cases of input currents, which indicates low density in the center region and high density in the peripheral region of plasma flame.

analyses carried out at central and peripheral regions of the diamond thin film deposited on the substrate with the following operation conditions, deposition time of 30 minutes, input current 500 A, and the same conditions for the rest as in the above case. The observation in Fig. 2 indicates that there are more graphite bonds than diamond bonds in the central region, while vice versa in the peripheral region. In other words, the H atom density is not enough to stabilize diamond bonds on the central region of the substrate. These results can be explained by the fact that a high-velocity stream of the arc jet keeps the injected reactant gases from penetrating effectively into the plasma flame center.

![Graphs](image)

(a) H density distributions and (b) C₂ density distributions for a case of far-injection method, where arc input currents are measured at 10.5 cm from the nozzle exit with Ar 32 l/min, H₂ 5 l/min, CH₄ 0.5 l/min and 160 Torr.

On the other hand, as shown in Fig. 3, the actinometry measurements for the case of far-injection method reveal somewhat uniform density distributions of major reactive...
species over the central region of plasma flame. These uniform density distributions are caused mainly by the enhanced mixing effects of reactant gases at the downstream of the plasma flame, where the stream velocity is relatively low. Thus, the far-injection method is expected to be preferable for getting the higher uniformity of the diamond thin film deposition.

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4. References

