Active Control of Nucleation Process in Plasma CVD by Ultra-Short High-Voltage Pulses

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Abstract

Effects of applying ultra-short high-voltage pulses on nucleation density in PACVD processes of diamond thin films has been examined by superposing the high voltage pulses on the usual DC plasma. The nucleation density is significantly enhanced by this method and could be controlled by only changing the pulse width. Enhancement of nucleation density arises from formation of stratified plasma structure with the high supersaturation of key radical species near the substrate of anode. The magnitude of the supersaturation degree is controlled by formation process of plasma structure depending on the pulse width.

1. Introduction

PACVD (Plasma Assisted Chemical Vapor Deposition) processes have been widely used in the manufacture of various thin films. However, it is difficult to control actively the quality of thin films under the processes by plasma properties. Ultra-short high-voltage pulses, which pulse width is less than one micro-second, have three advantages over conventional plasma generators in its controllability. First, its pulse width, pulse frequency and applied voltage can be easily controlled independently corresponding to the dissociative energy of source gas molecules, life time of key radical species and so on. Second, high radical yield can be obtained by high instantaneous power input. By this method, very high voltage up to several kV can be successfully applied under a glow plasma mode [1]. Because the pulse drops before the transition from the glow plasma mode to the arc. And third, it is possible to optimize the stratified plasma structure for the film depositions though a control of time dependent change of it.

In this study, the effect of applying the pulses on nucleation density in CVD process on diamond thin films has been examined by superposing the high voltage pulses on the usual DC plasma (pulse-superposing plasma). The nucleation density has been significantly enhanced by this method and could be controlled by only change of pulse width. Relationships between this phenomena and the structural change of plasma is discussed and a high possibility of the direct and active control under the processes by the pulse is demonstrated.

2. Experimental System and Procedure

The experimental apparatus used in this study is shown in Fig. 1 including the optical spectroscopy system to measure radical species. The ultra-short and high-voltage pulsed power has been generated by using the voltage wave propagation in a coaxial cable of fixed length [2]. The chamber has consisted of a quartz vessel. Electrodes for CVD diamond deposition are illustrated in details in Fig. 2. The upper electrode of cathode has been made of stainless which is 30mm in diameter, and the electrode distance has been set to 20mm. In order to increase of current density, the substrate of anode has been covered by insulating plate with hole which has been 5mm inside diameter.

The certain voltage-current waveforms of pulse-superposing plasma used for the deposition are shown in Fig. 3. The effect of pulse width on nucleation density have been examined by two type plasmas which pulse width have been different from 150ns to 400ns. The pulse frequency of both plasmas have been maintained to 120Hz. Silicon wafers used for semiconductor, which size have been 1×1cm², have been used as substrates. The experimental conditions for diamond deposition are shown in table 1. The diamonds deposited by these plasmas have been characterized for chemical bond-

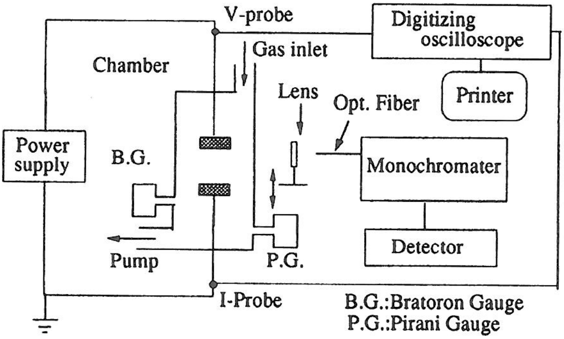


Fig. 1 Experimental system

Table 1. Experimental conditions for diamond deposition

	Pulse width (ns)	Gas	Pressure (kPa)	Electrode distance (cm)	Deposition time(min)	Flow rate (cm^3/min)
A	400	H_2(99%)− CH_4(1%)	6.7	2	30	50
B	150					
C	DC only					

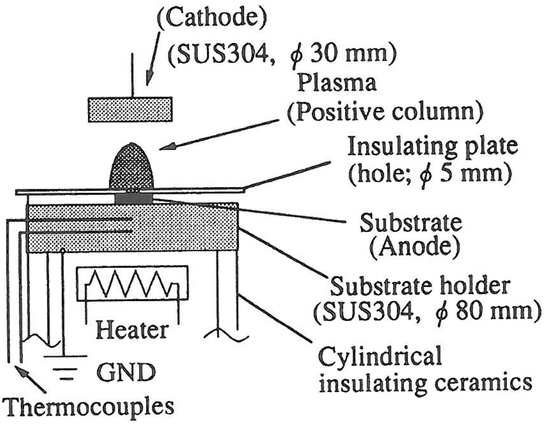


Fig. 2 Details of electrodes for diamond deposition

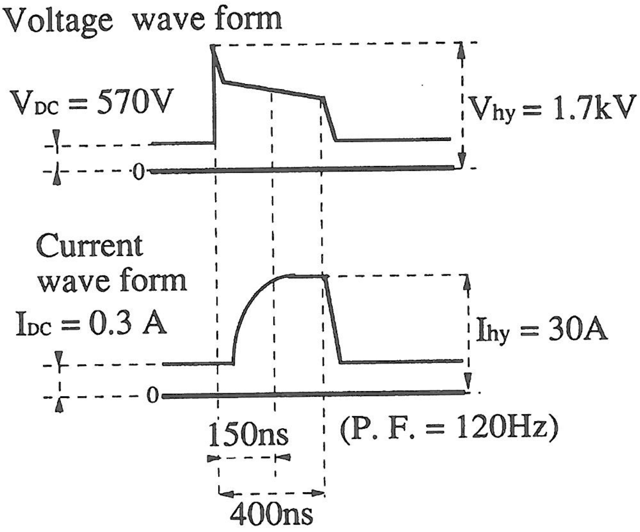
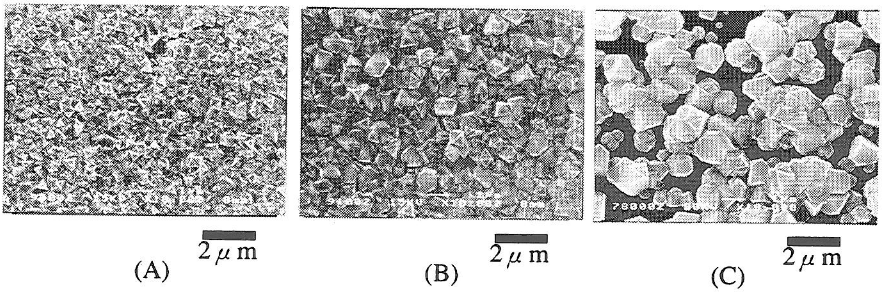


Fig. 3 Voltage and current waveforms of pulse-superposing plasma for diamond deposition

Table 2 Experimental conditions for optical measurement of time dependent change of pulse-superposing plasma

V_{hy}	I_{hy}	V_{dc}	I_{dc}	P.W.	P.F.	P	d	Gas (H_2/CH_4)	Flow rate
1.7kV	8A	570V	0.3A	600ns	1kHz	6.7kPa	3cm	99/1	50cm^3/min



(A) (B) (C)

Fig. 4 Surface morphology of films deposited under various plasma conditions

ing state and crystal structure by Raman spectroscopy and X-ray diffraction. On the other hand, the morphology of specimens have been also observed by SEM.

The time dependent change of plasma structure have been measured by emission intensity profiles of created radicals between electrodes. The experimental conditions for the measurement are shown in table 2. In order to clarify effect of applying pulses on the diamond deposition, the experiment has been operated under the condition close to the deposition use.

3. Deposition Experiments

Fig. 4 shows morphologies of diamond particles deposited by various plasma conditions. These figures indicate that the nucleation density has been increased by superposing pulses, and nucleation density has became greater as increasing pulse width. No difference of composition are among three specimens, which consist of high quality diamond.

In case of diamond deposition with DC plasma, the increase of current contributes the increase of particle or film grown rather than the enhancement of the nucleation processes [3]. On the other hand, the superposing pulses on DC plasma greatly enhanced nucleation process. Furthermore, this effect of superposing pulses are more drastically appeared for longer pulse width. This fact means that the magnitude of supersaturation degree is increased by high power input of the pulse and that it's controlled by the pulse width.

4. Time Dependent Change of Stratified Structure of Pulse-Superposing Plasma

Fig. 5 shows the time dependent change of H α emission intensity profiles of pulse-superposing plasma. Fig. 6 shows the H α emission intensity profile of DC plasma. These profiles of pulse-superposing plasma are quite different from that of DC plasma and shows a stratified structure with a strong luminescent positive column. While the DC plasma has an opposite structure with strongest luminescent zone in negative glow region near the cathode. In the case of pulse-superposing plasma, the emission intensity in the positive column increases until 150ns. And then the emission profiles in whole area keeps quasi-steady state until the end of pulse.

The emission of H α results mainly from dissociative excitation of H_2 by the electron collision. This reaction scheme may be reasonable under weakly ionized gas condition and flow system so that the degree of radicals creation relates with the emission intensity. The comparing of emission intensity between the pulse-superposing plasma and the DC plasma near the anode indicates that the instantaneous degree of radicals creation by pulse-superposing plasma are two orders higher than that by DC plasma. Therefore, enhancement of nucleation processes arises from the formation of plasma structure with the high supersaturation of key radical species near the substrate. Furthermore, the magnitude of the supersaturation is controlled by formation process of plasma structure depending on the pulse width.

However, it is rather hard to explain the increase of radicals density near the anode only by the increase of electron density without taking into account of change of

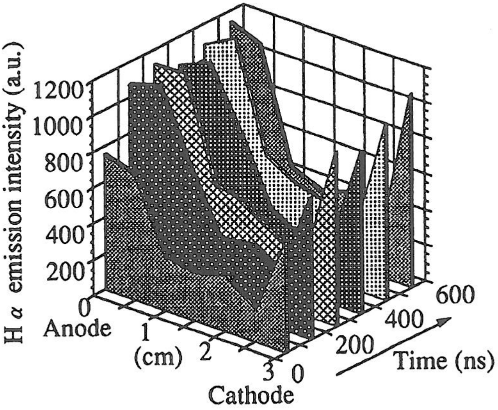


Fig. 5 Time dependent change of H α emission intensity profile in pulse-superposing plasma

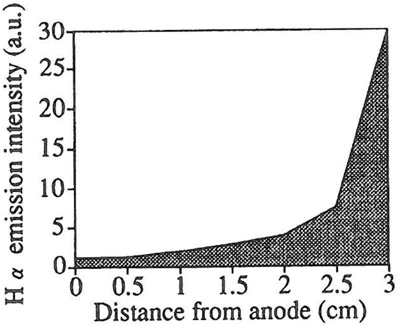


Fig. 6 H α emission intensity profile in DC plasma

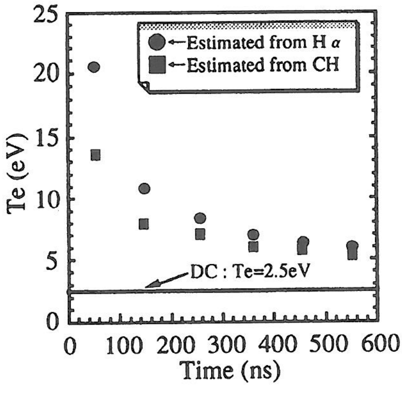


Fig. 7 Change of electron temperature in one pulse duration of pulse-superposing plasma

electron temperature. Because the ratio of the current of pulse-superposing plasma to that of DC plasma has been lower than the ratio of their emission intensities. This fact suggests that the electron temperature near the anode should have been highly elevated in the pulse-superposing plasma. The change of electron temperature in one pulse duration has been estimated by the emission intensities of radical species of CH and H α shown in Fig. 7. The electron temperature drastically increases just after the sharp rise of pulse voltage, and then gradually attenuates. Even after the attenuation, the electron temperature still remains higher than that of DC plasma (2.5eV [4]). It has been clarified that the increase of magnitude of supersaturation are caused not only by the increase of current but also by the higher electron temperature.

5. Conclusions

The nucleation density of diamond has been significantly increased by applying ultra-short pulse. This effect has appeared more drastically for longer pulse width due to the increase of radical density and its supersaturation degree near the anode substrate. The possibility of electron temperature control has been shown by change of electron temperature in applying pulse. This active control of PACVD process by use of the ultra-short high-voltage pulses could be much improved by optimizing a combination of pulse parameters based on further fundamental studies for deposition mechanisms.

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