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Formation of diamond films by pulsed discharge plasma chemical vapor deposition†

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Abstract

Diamond films were formed by pulsed discharge DC plasma chemical vapor deposition (CVD), wherein the discharge time (T_d) and nondischarge time (T_n) during each period of the pulse were changed. A subelectrode at a short distance from the cathode was also laid to provide stable discharge between the cathode and the substrate (anode). The discharge current (I_d) between the cathode and the substrate was controlled by the voltage of the pulsed power supply and by the bias voltage to the anode. The crystalline quality of the films deposited on the silicon substrate became superior when T_d decreased and T_n increased, although the deposition rate decreased. The optimum values of T_d and T_n to deposit high-quality film without decreasing the deposition rate were 0.5 and 2 ms, respectively. Corresponding to these structural changes, the emission intensity of the hydrogen (H_α and H_β) in the plasma increased when the deposition rate increased. The discharge was possible up to high P_g of about 300 torr and the crystalline quality and deposition rate were extremely improved when P_g was increased to about 200 torr The increase of the emission intensity of C_2 together with H_α and H_β was observed when P_g increased. The discharge at low I_d was also possible and could be deposited on small specimen such as fine tungsten wire of about 100 μm in diameter, which was used for field emission experiments. The field emission from the tungsten wire increased extremely when appropriate diamond film was coated. These results show that the crystalline quality and deposition rate can be controlled over a wide range by this method.

Keywords: Diamond film, pulsed discharge, plasma CVD, plasma emission spectroscopy, field emission.

1. Introduction

The DC plasma chemical vapor deposition (CVD) method at high gas pressures (P_g) of about 150 torr is an excellent method for depositing diamond film at relatively low substrate temperature (T_s).[1–4] The crystalline quality of the diamond film can also be improved by changing the waveform of the power supply from continuous DC to half-wave rectified.[5, 6] When a half-wave-rectified voltage is applied to the electrodes, the discharge becomes intermittent, and electron temperature and density become very high at the beginning of the discharge, showing that the gas decomposition efficiency is improved by this method. Furthermore, when the discharge is performed by pulsed power supply, the microstructure of the film can be controlled by means of changing duty ratio and repetitive period of the pulse.[7–10]

On the other hand, studies on the formation of diamond films by intermittent discharge plasma CVD show that the crystalline quality of the film becomes superior with increasing distance between electrodes from 10 to 20 mm. However, the discharge at longer electrode distance becomes quite unstable and sometimes impossible to start the discharge as the voltage becomes very high.

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Then, to maintain stable discharge at longer electrode distance, a subelectrode located closely to the cathode was introduced, and the substrate was biased with another DC power supply. The results of this method using subelectrode show that the crystalline quality of the film becomes superior when the electrode distance is about 20 to 25 mm, compared to 10 or 30 mm.[11] This method is also effective in changing the discharge current widely and to maintain the stable disc- harge at very low discharge current.

In this study, diamond films were prepared by pulsed discharge plasma CVD method using subelectrode. In the first phase, structural changes due to discharge time (T_d) and nondischarge time (T_n) were investigated by scanning electron microscopy (SEM) and Raman spectroscopy. The discharge at high gas pressure (P_g) became possible by this method, and then in the second, structural changes due to P_g were investigated. Spectroscopy studies of optical emission from the plasma during deposition confirm these results. The discharge at low I_d was also possible by this method, and then finally, deposited small specimens such as a fine tungsten wire of about 100 μm in diameter were deposited and the effect of coating to the field emission was investigated.

2. Structural changes due to discharge and nondischarge time

2.1. *Experimental method*

Figure 1 shows a schematic diagram of the CVD system used in the present experiments. After the chamber was pre-evacuated to about 10^{-6} torr, by turbo molecular pump, CH_4-H_2 gas mixture was supplied to the chamber. The $CH_4/(CH_4+H_2)$ ratio, i.e. methane concentration, was 3%. The gas pressure and the flow rate were 150 torr and 10 ccm, respectively. An Si wafer chip of about 5×5 mm was used as the substrate. The substrate was mounted on to the substrate holder (of about 10 mm in diameter) after being scrubbed with diamond paste and rinsed with acetone in an ultrasonic cleaner. The substrate was heated to 600°C and the deposition time was 2 h.

The cathode and the subelectrode were made of molybdenum plates of 0.2 mm thickness. The cathode was prepared by bending the molybdenum plate so that the bent tip becomes rounded and a cut chip of the molybdenum plate was used as the subelectrode. In the present experiments, the distance between the cathode and the subelectrode (L) was about 15 mm and about 20 mm between the cathode and the substrate (d).

The pulse power supply was fabricated by means of chopping the output of the DC power supply with IPM (intelligent power module) and elevating the voltage by a transformer (Fig. 2). The discharge time (T_d) and nondischarge time (T_n), which correspond to ON and OFF times of the IPM, were controlled by the pulse generator (PG).

When the pulsed voltage was applied to the cathode, where the substrate bias voltage (V_s) supplied from the DC power supply was zero, discharge took place between the cathode and the subelectrode, while no discharge was seen between the cathode and the substrate. The current from the pulse power supply (I_t) had a pulsed waveform and could be changed by changing the voltage from the power supply. When the positive substrate bias voltage (V_s) was increased under this condition, discharge between the cathode and the substrate began and became stronger with increasing V_s. Figure 3 shows typical waveforms of the discharge voltage (b) and current (c) between the cathode and the substrate, corresponding to the waveform of the PG (a). The dis-

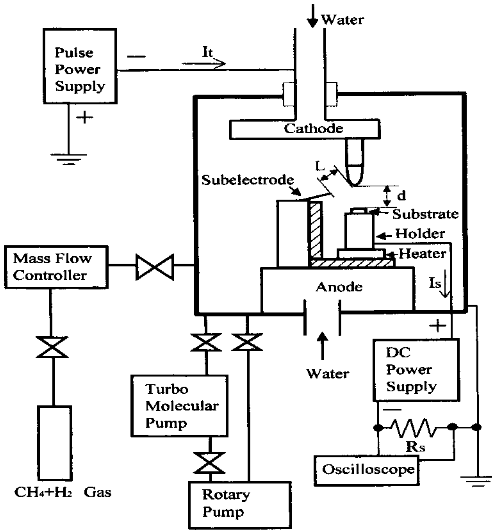

FIG. 1. Scheme of pulsed discharge plasma CVD system using subelectrode.

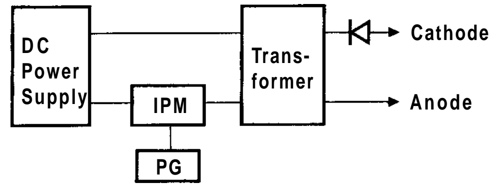

FIG. 2. Scheme of pulsed power supply. Output of DC power supply is chopped by IPM (intelligent power module) controlled by PG (pulse generator).

charge voltage increases to threshold (V_p) of about 700 V initially and then decreases to V_d of about 400 V. The discharge current increases to I_s after threshold level, and decreases after T_d. The strength of I_s could be changed both by output voltage of the pulsed power supply and V_s.

Figure 4 shows the change in I_s when V_s is changed, where $T_d = 0.5$ ms and $T_n = 2$ ms and the current from the pulse power supply at $V_s = 0$ (I_{to}) is changed from 0.5 to 1 A. The discharge between the cathode and the substrate begins at around $V_s = 300$ V and I_s can be changed from about 0.5 to 1.2 A. Because of the stable discharge between the cathode and the subelectrode, the discharge between the cathode and the substrate became stable at the wide range of I_s.

2.2. *Structural changes due to discharge time (T_d)*

Figure 5 shows SEM micrographs on the surfaces of the samples when T_d is changed from 0.75 to 0.25 ms under a constant T_n of 2 ms. The discharge current (I_s) denoted in Fig. 3 is 0.75 A. When T_d is decreased from 0.75 to 0.5 ms, grains in the film develop clear crystal growth habit, and when further decreased to 0.25 ms, become sparse. Figure 6 shows Raman spectra of the samples shown in Fig. 5. In agreement with the results of SEM shown in Fig. 5, the peak at 1333 cm^{-1} of diamond becomes strong and sharp when T_d is decreased from 0.75 to 0.5 ms. When further decreased to 0.25 ms, the broad peak of the amorphous component sifts from around 1500 to 1400 cm^{-1}, though the peak of diamond becomes small. The results show that the crystalline quality of the film becomes superior when T_d is decreased to 0.5 ms, and the deposition rate decreases when further decreased to 0.25 ms.

2.3. *Structural changes due to nondischarge time (T_n)*

Figure 7 shows SEM micrographs on the surfaces of the samples when T_n is changed from 1 to 2.5 ms under a constant T_d of 0.5 ms. The other deposition conditions are the same as those of the

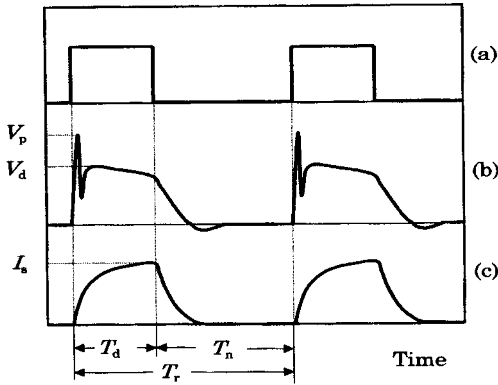

FIG. 3. A typical waveform of PG. (a) discharge voltage (b) and current (c) between the cathode and the substrate.

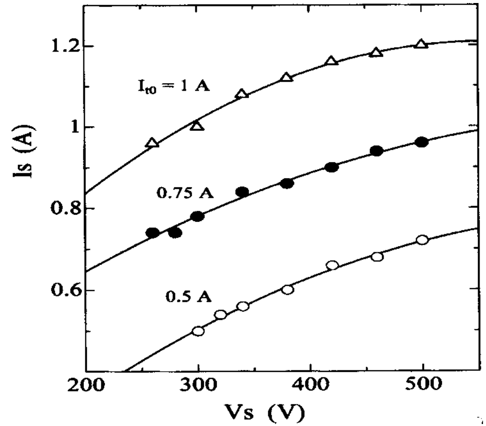

FIG. 4. Change of discharge current (I_s) when substrate voltage (V_s) is changed, where current (I_{to}) from pulse power supply at V_s= 0 is changed from 0.5 to 1 Å.

samples shown in Figs 5 and 6. When T_n is increased from 1 to 2 ms, grains in the film come to have clear crystal habit, and when further increased to 2.5 ms, become sparse. Figure 8 shows Raman spectra of the samples shown in Fig. 7, when T_n is changed from 1 to 2 ms. In agreement with the results of SEM shown in Fig. 7, the peak of diamond at 1333 cm^{-1} becomes strong and sharp with increasing T_n. These results show that the crystalline quality of the film becomes superior when T_d is increased to 2 ms, and the deposition rate decreases when T_d is further increased to 2.5 ms.

2.4. *Emission spectra from plasma*

Spectral intensity of plasma during deposition was measured to estimate the structural changes due to T_d and T_n. Strong peaks of H_α at 656 nm and H_β at 486 nm, and weak peaks of H_γ at 434 nm, CH at 431 nm and C_2 at 516 nm were observed. When T_d and T_n were changed, the emission intensity of $H_\alpha(I_{H\alpha})$ and $H_\beta(I_{H\beta})$ was fairly changed, though the changes in the weak peaks were not clear.

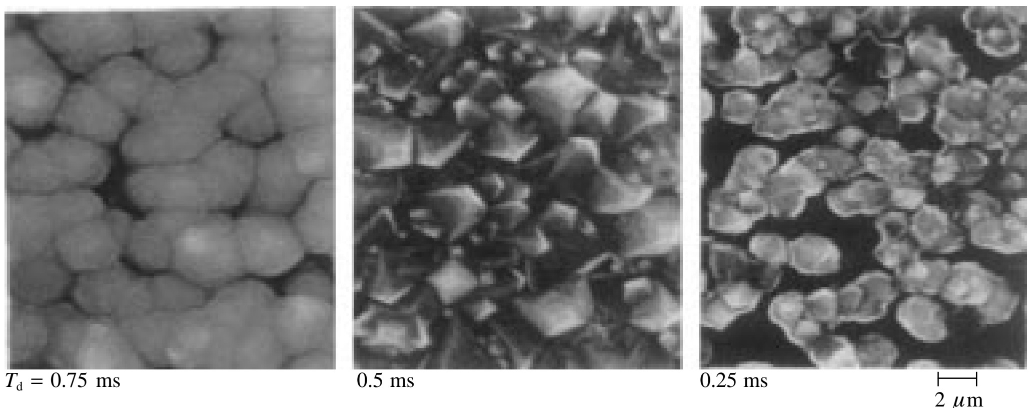

FIG. 5. SEM micrographs on the surfaces of the samples when the discharge time (T_d) is changed from 0.75 to 0.25 ms. Nondischarge time (T_n) is 2 ms.

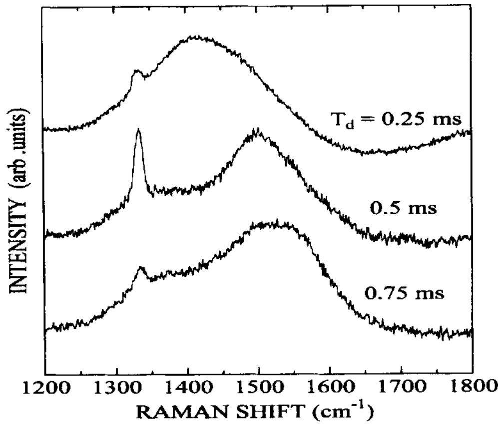

FIG. 6. Raman spectra of the samples shown in Fig. 5.

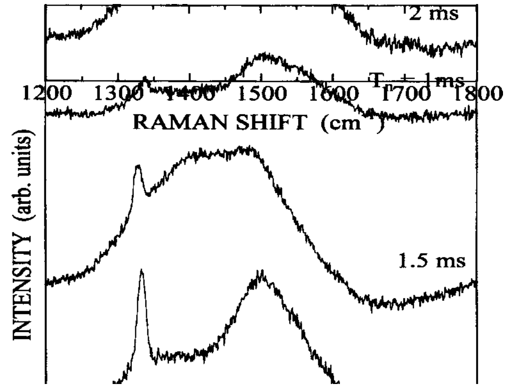

FIG. 8. Raman spectra of the samples shown in Fig. 7 when T_n is changed from 1to 2 ms.

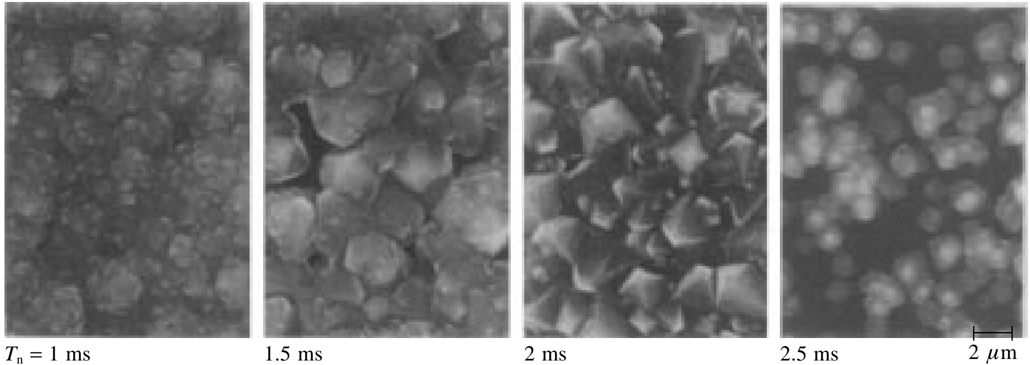

FIG. 7. SEM micrographs on the surface of the samples when T_n is changed from 1 to 2.5 ms under a constant T_d of 0.5 ms.

Table I shows the changes in $I_{H\alpha}$ and $I_{H\beta}$ when T_d is changed, where the intensity is normalized so that the highest value becomes 100%. When T_d is decreased from 0.75 to 0.50 ms, the decreases in $I_{H\alpha}$ and $I_{H\beta}$ are small, but become considerably large when further decreased to 0.25 ms. Then these decreases correspond to the decrease of the deposition rate shown in Fig. 5 and suggest that atomic hydrogen has important role to play in the growth of diamond.[12]

Table II shows the changes in $I_{H\alpha}$ and $I_{H\beta}$ when T_n is changed from 1.0 to 3 ms, where the intensity is normalized so that the maximum value becomes 100%. When T_n is increased from 1.0 to 2.0 ms, the decreases in $I_{H\alpha}$ and $I_{H\beta}$ are small. However, when increased from 2.0 to 2.5 ms, the decreases become considerable. The decreases of $I_{H\alpha}$ and $I_{H\beta}$ correspond to the decrease of the deposition rate shown in Fig 7.

Table I
Emission intensities of $H_\alpha (I_{H\alpha})$ and H_β $(I_{H\beta})$ of the plasma, when discharge time (T_d) is changed from 0.75 to 0.25 ms. The $I_{H\alpha}$ and $I_{H\beta}$ are normalized so that the maximum value becomes 100%.

T_d (ms)	$I_{H\alpha}$(%)	$I_{H\beta}$(%)
0.75	100	100
0.50	95	98
0.25	67	73

Table II
Emission intensities of H_α $(I_{H\alpha})$ and H_β $(I_{H\beta})$ of the plasma, when nondischarge time (T_n) is changed from 1.0 to 3.0 ms. The $I_{H\alpha}$ and $I_{H\beta}$ are normalized so that the maximum value becomes 100%.

T_n (ms)	$I_{H\alpha}$(%)	$I_{H\beta}$ (%)
1.0	100	98
1.5	100	100
2.0	96	99
2.5	85	90
3.0	75	80

3. Structural changes due to gas pressure (P_g)

3.1. *Experimental*

By using the subelectrode mentioned above, the discharge at high gas pressure (P_g) became possible and the crystalline quality also improved extremely when P_g was risen to above 200 torr.

In this experiment, on the structural changes due to P_g, the thermocouple located near the substrate could not be used at high P_g because of arc discharge to the thermocouple, and the substrate temperature (T_s) was measured by an optical thermometer. The measured T_s was about 900°C, and the methane concentration was 1%. The other experimental method is similar to those mentioned in Section 2.1.

3.2. *Structural changes*

Figure 9 shows SEM micrographs on the surfaces of the samples when P_g is changed from 150 to 300 torr. The discharge current (I_s) denoted in Fig. 3 is 1 A. The discharge time (T_d) and nondischarge time (T_n) are 0.5 and 2 ms, respectively. When P_g is increased from 150 to over 200 torr, grains in the film develop clear crystal growth habit. Figure 10 shows Raman spectra of the samples shown in Fig. 9. In agreement with the results of SEM shown in Fig. 9, the peak of the diamond at 1333 cm^{-1} becomes strong and sharp when P_g is increased from 150 to 200 torr. These results show that crystalline quality of the film becomes superior when P_g is increased to more than 200 torr.

3.3. *Optical emission from plasma*

Figures 11 (a) and (b) show changes in the emission intensity of H_α $(I_{H\alpha})$ and H_β $(I_{H\beta})$, respectively, when T_n and P_g are changed, under a constant T_d of 0.5 ms. When P_g is increased from 150 to 300 torr, these emission intensities increase. When T_n is increased to 2 ms, the decreases of $I_{H\alpha}$ and $I_{H\beta}$ are small. These decreases become considerably large when T_d is further decreased. This tendency is similar to the results mentioned in Section 2.4.

Figure 11(c) shows changes in the emission intensity of C_2 when T_n and P_g are changed. The intensity of C_2 decreases when T_n increases and increases with increasing P_g and becomes comparable to $I_{H\beta}$. The improvement of crystalline quality shown in Figs 9 and 10 may be caused by increase in C_2.

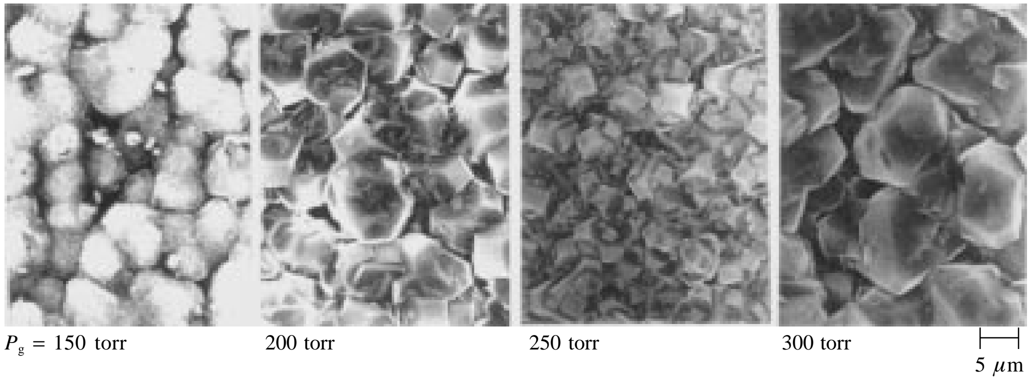

FIG. 9. SEM micrographs on the surfaces of the samples when gas pressure (P_g) is changed from 150 to 300. T_d and T_n are 0.5 and 2 ms, respectively.

4. Field emission

In this method, the discharge at small current is possible, and can deposit the diamond films on to the small substrate. In this experiment, the diamond films were deposited on a fine tungsten wire of 100 μm in size and the characteristics of the field emission were measured. The discharge current (I_s) was 0.4 A, and the methane concentration was 3%. The measurement of the field emission was performed at Nagoya Institute of Technology.[13,14]

Figure 12 shows SEM micrographs of the fracture surface of the sample deposited on the tungsten wire. The repetition period and duty ratio of the pulsed discharge current were 5 ms and 20%, respectively. The diamond film is coated uniformly on the tungsten wire.

The effect of the diamond coating on the field emission was investigated by using the samples prepared by changing the deposition conditions. The results showed that the emission did not

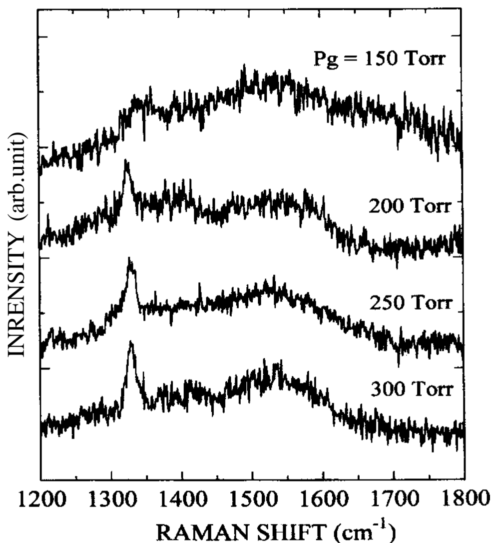

FIG. 10. Raman spectra of the samples shown in Fig. 9, where P_g is changed from 150 to 300 torr.

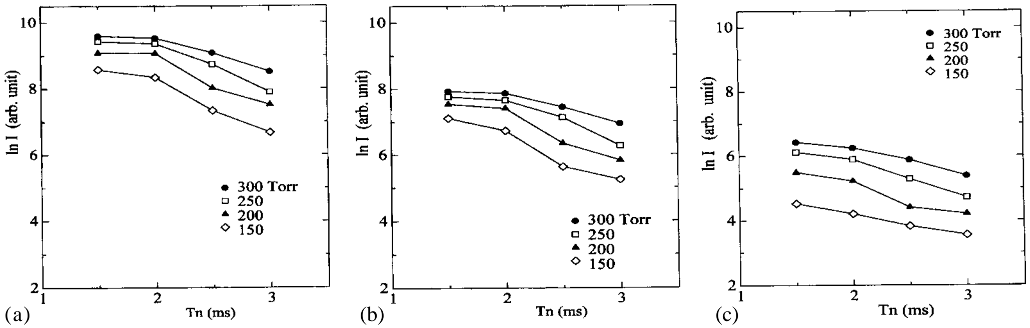

FIG. 11. Change of emission intensity of (a) H_α, (b) H_β and (c) C_2 when T_n is changed from 1.5 to 3 ms, and gas pressure P_g is changed from 150 to 300 torr.

occur when the crystalline quality of the coated film was superior, and considerable improvement was observed when inferior film was coated.

Figure 13 shows the field emission characteristic of the tungsten wire and the samples coated with low-quality diamond film. The repetition frequency, duty ratio and current (I_s) were 200 Hz, 30% and 0.4 A, respectively. The gap between the sample and the electrode was 0.05 mm. The emission current of the tungsten wire was not observed at room temperature. The emission current of the sample coated with the diamond film flows as shown in the figure. When the tungsten wire is heated to 1000 K, the emission current begins to flow at the applied voltage of about 1700 V. While the emission current of the coated sample begins to flow at lower voltage of about 800 V, the value of the current becomes extremely large. Then, the field emission from the tungsten wire is vastly improved by the coating of the appropriate diamond film.

4. Summary

Diamond films have been formed by pulsed discharge plasma CVD, wherein T_d and T_n in each period are changed and a subelectrode located closely to the cathode is introduced to perform stable discharge between the cathode and the substrate. The discharge current (I_s) between the cathode and the substrate can be controlled widely by changing the output of the pulse power supply and bias voltage to the substrate. The crystalline quality of the film becomes superior when T_d decreases and T_n increases. The deposition rate decreases when T_d decreases less than 0.5 ms

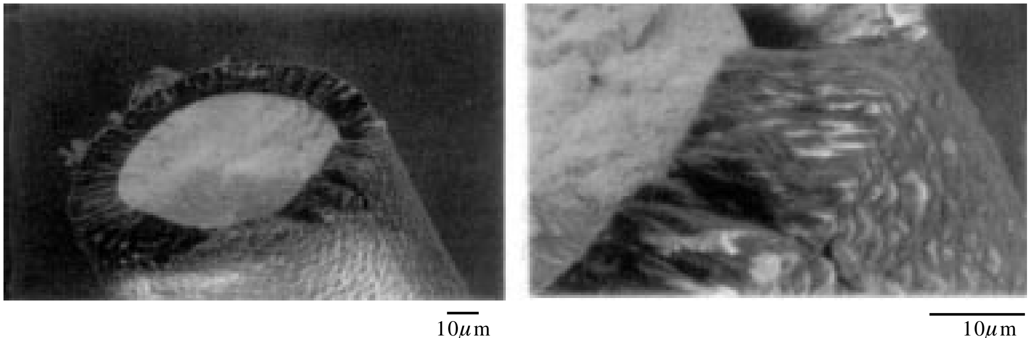

FIG. 12. SEM micrographs of the fracture surface of the sample deposited on the tungsten wire.

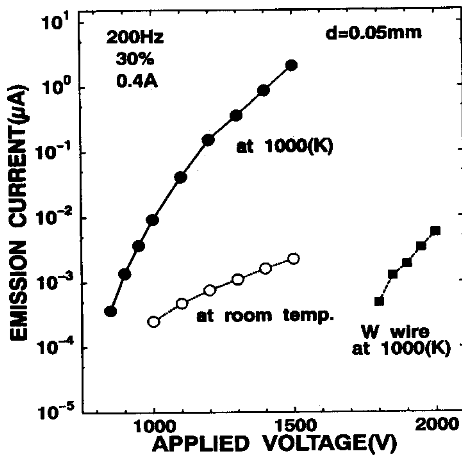

FIG. 13. Field emission characteristic of the tungsten wire and the sample coated with low-quality diamond film. The measurement was performed at room temperature and at 1000 K. The repetition frequency, duty ratio and current of the deposition of the diamond film were 200 Hz, 30% and 0.4 A, respectively, The gap between the sample and the electrode was 0.05 mm.

and T_n increases more than 2 ms. The optimum value of T_d and T_n to deposit high-quality film without decreasing the deposition rate are 0.5 and 2 ms, respectively. The emission intensities of H_α and H_β from the plasma decrease when the deposition rate decreases. The discharge is possible up to high P_g of about 300 torr, and the crystalline quality and deposition rate are extremely improved when P_g is increased to more than 200 torr. The increase in the emission intensity of C_2 together with H_α and H_β is observed when P_g increases. The discharge at low I_d was also possible and can deposit on small specimen such as fine tungsten wire of about 100 μm in diameter. The field emission from the tungsten wire is extremely improved by the coating of the low-quality diamond film.

These results show that the crystalline quality and deposition rate can be controlled over a wide range by this method and can use for various kinds of coating.

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