Transactions of the Materials Research Society of Japan 31[2] 467-470 (2006)

Synthesis of Carbon Nanomaterials Using Pulse Microplasma

Q. Zou, H. Yoshimura, A. Hatta
Department of Electronic and Photonic Systems Engineering, Kochi University of Technology
185 Miyanokuchi, Tosayamada-cho, Kami-gun, Kochi 782-8502, Japan
Fax: +81-887-57-2120, e-mail: 096406b@gs.kochi-tech.ac.jp

Synthesis of carbon nanomaterials by pulse microplasma in a scanning electron microscope (SEM) chamber equipped with a special discharge cell was illustrated. The peak current density of the CH_4 microplasma was higher than 5 kA/cm^2 and the pulse width was almost 10 ns. There were some carbon nanomaterials deposited besides source-melted spots on the cathode of platinum film after 5 s operation.
Key words: Microplasma, Pulse Discharge, Carbon, Nanomaterial

1.INTRODUCTION

Recently, microplasma has been intensively studied because of its interesting characteristics of small volume, low energy consumption and high density, and application on flat panel displays in various fields such as analytical instrumentation and materials processing [1]. Study on microplasma discharges operated in a SEM chamber is reported in this paper. It was found that the discharges pulsed automatically when a DC high voltage was applied through a high resistance to electrodes with a gap from 10 to 100 μm at near atmospheric pressure. When the peak current density of the pulse discharge reached 5 kA/cm^2, the electrodes were not seriously damaged due to short duration of pulse width, i.e. 10 ns. In this work, it is demonstrated that carbon nanomaterials appear on the cathode when the pulse microplasma is operated in the presence of CH_4 gas.

2.EXPERIMENTAL DETAILS

Microplasma discharges were carried out in a removable gas cell installed in a SEM (Hitachi, S-3000N) chamber, as shown in Fig.1. A platinum film (about 600 nm thick) deposited on an n-Si (100) wafer was used as the cathode and a palladium alloy needle of 12 μm tip curve rate was used as the anode. The gap between the anode and cathode was adjusted while observing the SEM image, as shown in Fig.2. After setting the electrodes, the gas cell was closed and was filled with CH_4 gas up to 100 kPa.

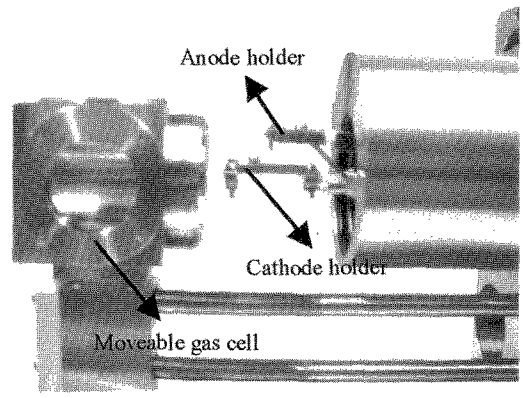

Fig.1 Microplasma discharge cell in SEM

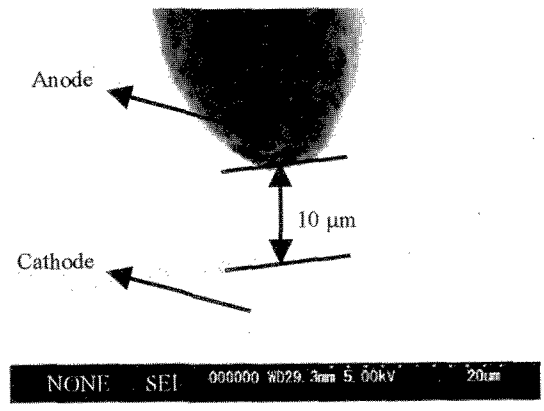

Fig.2 SEM image of the anode and cathode

To avoid serious damage of the electrode, a relatively high resistor was inserted in the circuit to provide a high voltage to the anode, as shown in Fig.3. The high voltage power source was operated in pulse modulation at 10 Hz frequencies and 0.6% duty ratio. The anode voltage and the cathode current were monitored by a digital oscilloscope (Lecroy LT364) of a 500 Ms/s and a 400 MHz bandwidth.

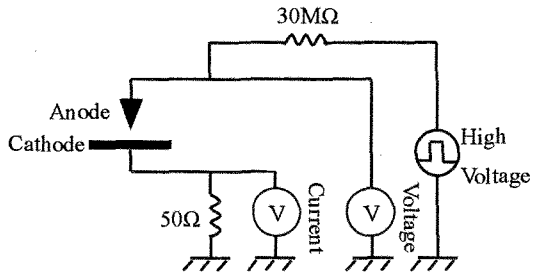

Fig.3 Circuit of experiment

A FESEM (JEOL, JSM-7400F) and a SEM were used to observe the surface of electrodes before and after discharge. Energy dispersive X-ray spectroscopy (EDX) was used to determine the components of the material.

3.RESULTS AND DISCUSSION

Fig.4 shows typical waveforms of voltage and current when the gap was 50 μm and CH_4 pressure was 100 kPa. An initial discharge of a large current and about 16 times of repeating discharges occurred during each pulse, as shown in Fig.4. The peak current was higher than 1.5 A and the pulse width was almost 10 ns during the initial discharge. Because the current was terminated by a 50 Ω terminator, current higher than 1.5 A was beyond the range of oscilloscope.

Fig.5 shows FESEM images of the discharge area on the cathode surface after 5 s of operation at 50 μm gap and 100 kPa pressure. There were nearly 40 spots in the area, as shown in Fig.5 (a). Eleven spots are clustered in the center. Fig.5 (b) shows a high magnification image of the square area in Fig.5 (a). The platinum cathode surface melted locally in the center and at the spots. During the 5 s 10 Hz operation, 50 large current discharges and nearly 1000 small current discharges were observed in the current waveform. The number of melted spots approximately coincides with the number of large current

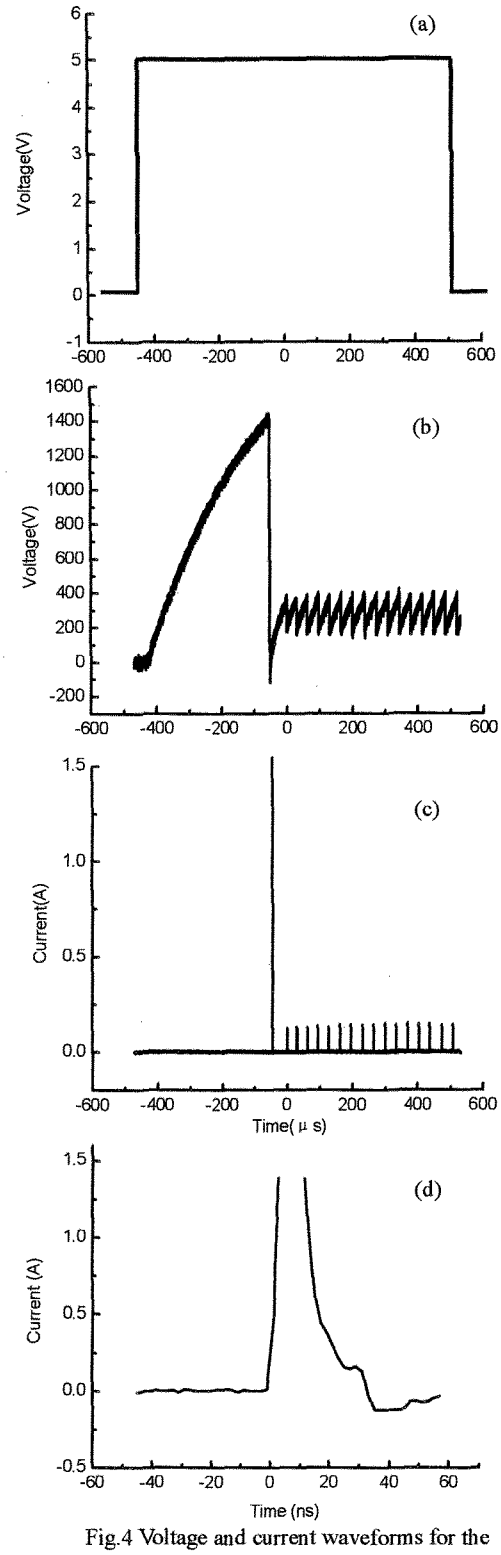

Fig.4 Voltage and current waveforms for the CH_4 100 kPa pressure and 50 μm gap gas discharge (a)Applied pulse high voltage, (b) Anode monitored voltage, (c) Cathode current, (d) Current of the initial discharge in a pulse on the expanded time

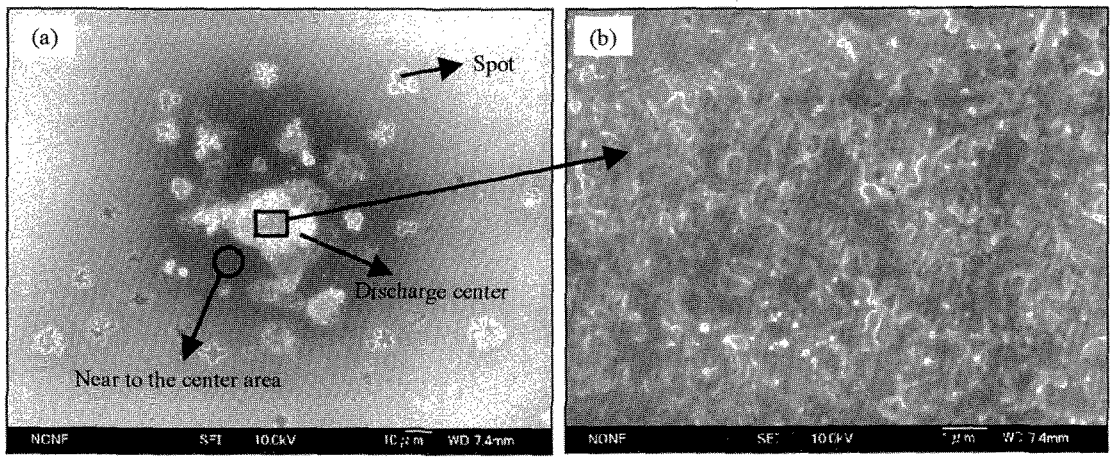

Fig.5 FESEM images of cathode surface after 5 s deposition of discharge when gap was 50 μm and pressure was 100 kPa (a) Low magnification image of discharge area, (b) High magnification of square area in (a)

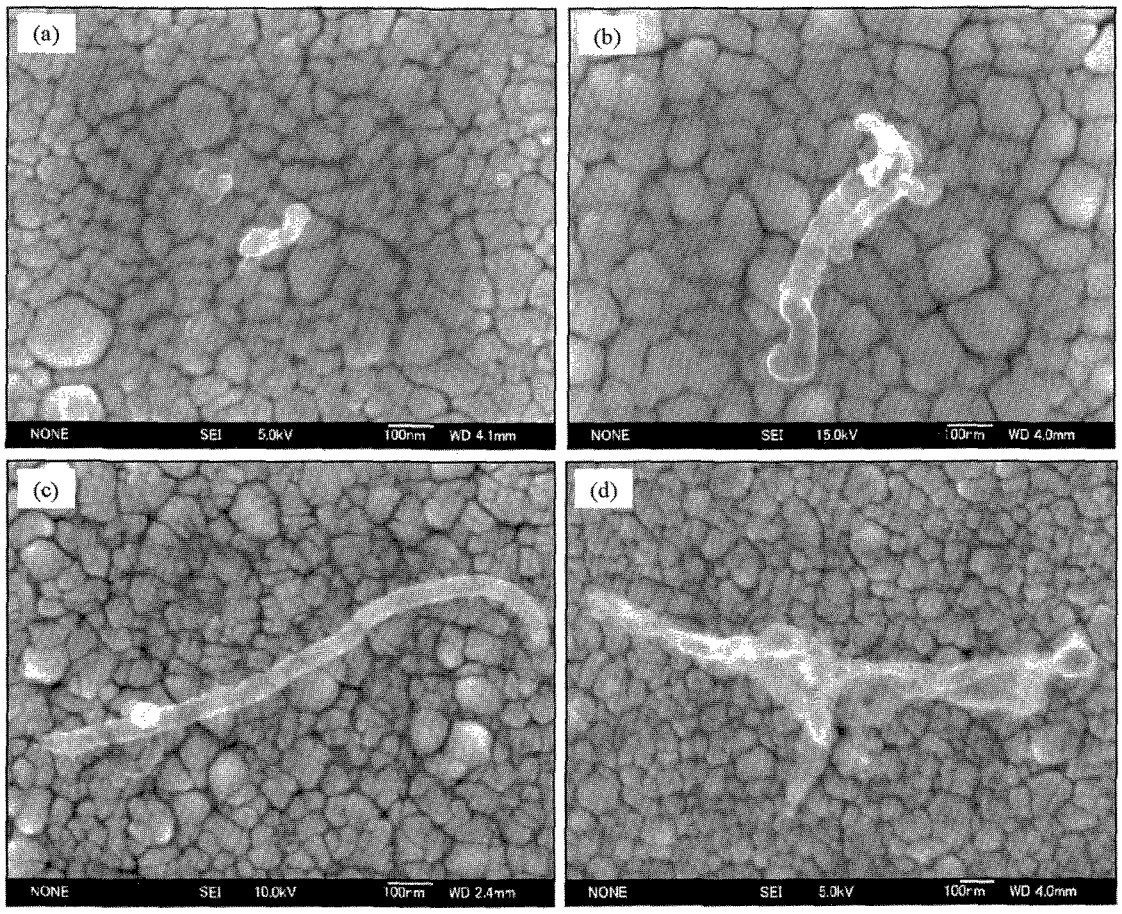

Fig.6 FESEM images of cathode surfaces after different time operation discharge when gap was 50 μm and pressure was 100 kPa (a) 1 s, (b) 3 s, (c) 5 s and (d) 10 s

discharges.

Fig.6 shows FESEM images of some products found on the cathode after CH_4 discharge when the gap was 50 μm and pressure was 100 kPa. All the images were taken in the area (the circle area) near the center area, as shown in Fig.5 (a). The images show that there were two kinds of materials on the surfaces of cathode after operation.

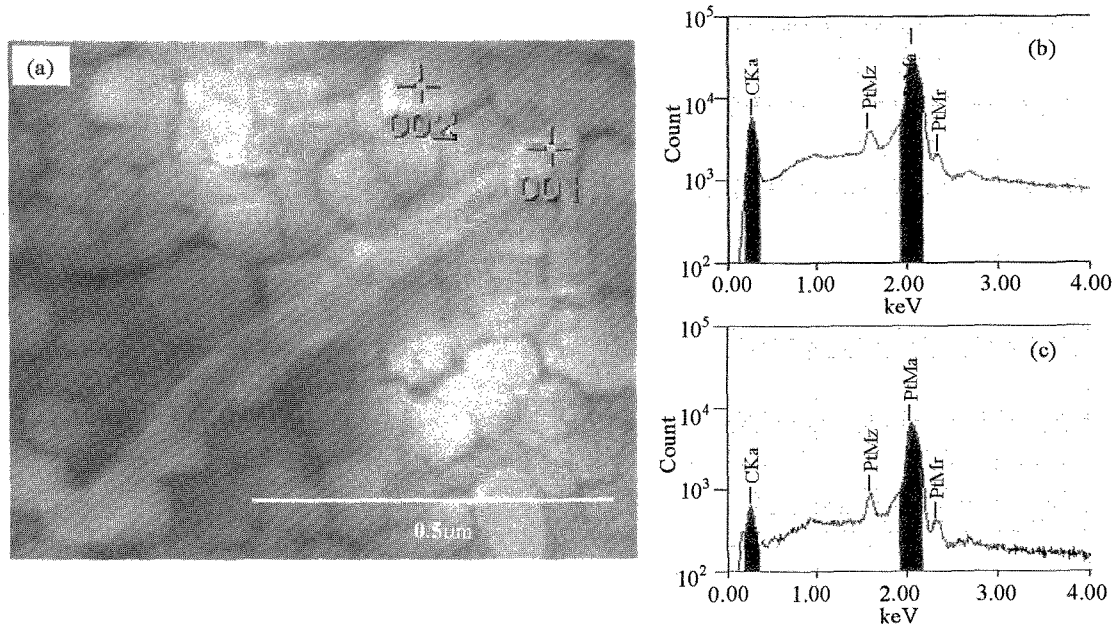

Fig.7 EDX of cathode surface after 5 s operation of discharge when gap was 50 μm and pressure was 100 kPa (a) FESEM image of the measured spots, (b) 001 spot- nanomaterial spot and (c) 002- non-nanomaterial spot

One is platinum with most grains almost 30 nm in diameter, and the other is a carbon nanomaterial. Fig.6 (a) shows the FESEM image of 1 s. The typical length and diameter of these nanomaterials were 100 nm and 30 nm, respectively. Fig.6 (b) shows the FESEM image of 3 s. The typical length of the nanomaterial were almost 300 nm, which is longer than that obtained at 1 s. In Fig.6 (c) the FESEM image of 5 s is shown. Here the typical length and diameter of the nanomaterial was approximately 800 nm and 30 nm, respectively. When the deposit time was longer than 5 s, the nanomaterials melted, as shown in Fig.6 (d).

Fig.7 shows the EDX results of the cathode surface after a 5 s operation at 50 μm gap and 100 kPa pressure. The measured spots are shown in Fig.7 (a). It is clear that the carbon content of the nanomaterial spot was higher than that of the non-nanomaterial spot.

It is estimated, from the initial discharge current waveform shown in Fig.4 (d) and the discharge area shown in Fig.5, that the current density is approximately 5 kA/cm^2 when the gap was 50 μm and pressure was 100 kPa. Fig.6 suggests that the length of the nanomaterial increases with the operation time increasing up to 800 nm at 5 s when the gap was 50 μm and pressure was 100kPa.

CONCLUSIONS

Pulse microplasma discharges were operated with CH_4 at near atmospheric pressure using a thick (about 600 nm) polycrystalline platinum film cathode and a palladium alloy needle anode. No serious thermal damage on the surface of polycrystalline platinum film occurred after discharge for 5 s. Carbon nanomaterials were found on the cathode. The diameter of the carbon nanomaterials was approximately 30 nm and the length increased when the operating time increased up to 800 nm at 5 s.

ACKNOWLEDGEMENT

This work was supported by a Grant-in-Aid for Specific Research of Priority Areas "Generation of Micro-scale Reactive Plasmas and Development of Their New Applications" (#15075209) from the Ministry of Education, Culture, Sports, Science and Technology.

REFERENCE

[1] Kazuo Terashima, Tsuyohito Ito, Ken Katahira and Taka-aki Tomai, Appl. Phys. Lett. , 80(2002)37.

(Received December 23, 2005; Accepted February 20, 2006)