

# Development of cross-flow micro-nebulizer for atmospheric pressure microplasma deposition and its application to prepare nano-carbon materials from alcohol

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Compact cross-flow micro-nebulizer system was developed to introduce the liquid raw materials into the atmospheric-pressure microplasma deposition system, which can control the feed rate of liquid sample to be less than 30  $\mu\text{l}/\text{min}$ . As the first study of the injection of liquid raw material, ethanol or ferrocene/ethanol solution was introduced through the developed nebulizer system to deposit nano-carbon materials, and carbon nanoions (CNOs) and carbon nanotubes (CNTs) were deposited selectively on the localized area of the glass-epoxy substrate kept toward the downstream of the microplasma jet. The reaction processes during the deposition were discussed based on the optical emission spectroscopy, which strongly indicates the role of OH radicals from the decomposition of ethanol for the selective formations of the CNO and CNTs.

Key words: microplasma, atmospheric-pressure, micro-nebulizer, carbon nano-ion, carbon nanotube, ethanol

## 1. INTRODUCTION

Atmospheric-pressure microplasma jet is a powerful tool for deposition of materials on a substrate [1-4] as well as etching [5-6] on a specified local area on a substrate. In material processing, the microplasma technique is able to protect low-melting point substrate from thermal damage because of the low heat capacity and heat flux, which are proportional to the mass of the heat source [7]. As far as deposition technique is concerned, the most of the developed techniques are based on chemical vapor deposition (CVD) using only gas source, and the kinds of deposition materials are very limited accordingly. To extend the variety of deposition materials, we had developed the following technique for metal oxide deposition up to now; The  $\mu\text{m}$ -diameter metal wire, inserted into the microplasma generation nozzle (quartz tube), is evaporated by microplasma and reacted with etched oxygen from the quartz tube, finally the generated species are condensed to form metal oxide grains [7]. In this method, the reaction between solid raw material and gas source is dominant.

Recently, we have developed a compact cross-flow micro-nebulizer\* to introduce the liquid raw material into the microplasma deposition system. This system is mainly composed of the commercially available stainless connector and some couplings, and able to join directly to the upstream of the microplasma generator which we have developed so far [3,7]. In this system, the feed rate of liquid sample can be controlled to be less than 30  $\mu\text{l}/\text{min}$  (about 5~30  $\mu\text{l}/\text{min}$ ), and thus the stable generation of the microplasma can be kept even after supplying of the liquid sample. In addition, this development can enable to extend the variety of deposition materials in future, because it is possible to use the suspension containing the fine powders as a source material. As a first study of the injection of liquid raw material, ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) or ferrocene ( $\text{Fe}(\text{C}_5\text{H}_5)_2$ )/ethanol solution was introduced to the atmospheric-pressure microplasma through the developed nebulizer system to deposit nano-carbon materials. In this method, onion-like nano-carbon (carbon nano-onion; CNO) and carbon nanotube (CNT) were deposited efficiently on the localized area of the glass-epoxy substrate kept toward the downstream of the microplasma jet. This result is quite different from previous reported one way; CNTs were prepared only on the inserted metal wire by supplying of methane gas ( $\text{CH}_4$ ) and vaporized ferrocene into the microplasma generation nozzle, and

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### Footnote

\* Cross-flow means the direction of the liquid sample feed nozzle is perpendicular to the nebulizing gas flow direction. Micro-nebulizer means the amount of the nebulized liquid sample is micro-litter ( $\mu\text{l}$ ) /min.

never obtained on the substrate out of the nozzle [8]. In addition, their yield was high and formed by products such as graphite-sheet, amorphous carbon, and polyhedral-shaped nano-carbon were rarely observed although the mixture of amorphous and polyhedral nano-carbons were obtained from  $\text{CH}_4$  gas [3]. These results suggest that the alcohol is the suitable carbon source material for localized deposition of CNOs and CNTs with a higher yield using an atmospheric-pressure microplasma jet.

In this paper, we report the details of the developed cross-flow micro-nebulizer for atmospheric-pressure microplasma deposition and the results of the deposition obtained from ethanol or ferrocene /ethanol solution. The reaction processes occurred in the microplasma during deposition are discussed based on an optical emission spectroscopy (OES). This measurement strongly indicates the role of OH radicals from the decomposition of ethanol, which was already suggested in literature [9], and enabled to explain the high-yield preparation of CNO from ethanol.

## 2. DETAILS OF THE CROSS-FLOW MICRO-NEBULIZER

We developed the simple and small nebulizer system which is able to keep the simplicity of the microplasma apparatus even after the connection of the nebulizer. Most of this nebulizer body is made up of the commercially available stainless T-connector for 1/4 inch (in.) outer diameter (o.d.) tubes and some coupling. The cross-sectional drawing of the nebulizer is depicted schematically in Fig. 1. The liquid flow nozzle was made by fine-drawing of the quartz-tube. The tip inner diameter (i.d.) of the nozzle is the critical dimension to control the feed amount of the sample, which depends on the drawing conditions. In this study, the nozzle of about 10  $\mu\text{m}$  tip i.d. was employed. This nozzle is fixed to the metal tube (o.d. : 1/8 inch), which is inserted in the Tygon tube<sup>®</sup> (i.d. : 1/8 inch, o.d. : 1/4 inch) and tightly gripped by coupling with a ferrule and a nut. The other end of the Tygon tube<sup>®</sup> is connected to the source materials container. The plasma gas of Ar, which is used as also the nebulizing gas, flows in the direction perpendicular to the liquid flow feed nozzle. The 1/8 in. o.d. tube for plasma gas feed is inserted up to the 5 mm in front of the liquid nozzle to nebulize the liquid raw material effectively at a higher gas speed.

## 3. EXPERIMENTAL

### 3.1 Atmospheric-pressure microplasma generator

In this study, a few modifications were made on the original setup of microplasma generator depicted in literature [7]. The modified setup is depicted schematically in Fig. 2. The pinched quartz nozzle, whose tip i.d. is about 50  $\mu\text{m}$ , was used as a plasma

generation nozzle. A 10-turn coil made of 550- $\mu\text{m}$  diameter Cu wire was looped around the zone of 10 mm from the tip. The coil one end was connected to a 450 MHz UHF (Ultra High Frequency) generator via matching circuit, while the other end was floated. Molybdenum wire of 100  $\mu\text{m}$  diameter was inserted into the pinched nozzle area, where i.d. of pinched zone is about 150  $\mu\text{m}$ . The other end of wire was affixed to the inner wall of the metal tube (o.d., 1/8 inch), which is connected to the nebulizer via reducing coupler (1/8 in. o.d. – 1/4 in. o.d.).

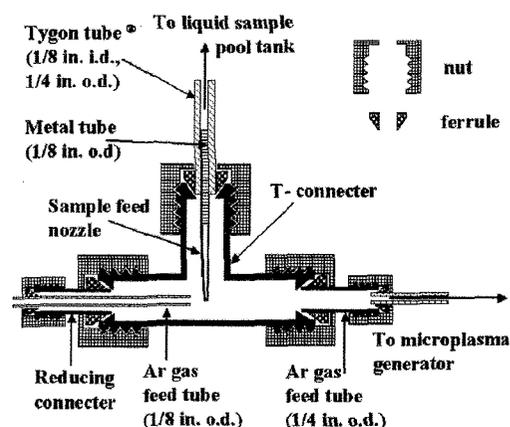


Fig.1 A cross-sectional drawing of the developed micro-nebulizer.

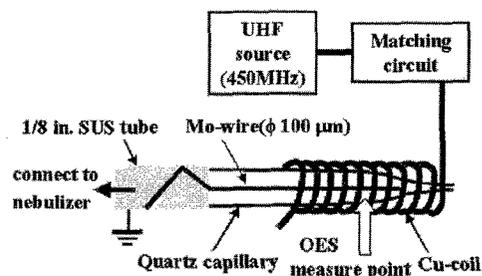


Fig.2 A schematic diagram of the atmospheric pressure microplasma generator.

### 3.2 Deposition and characterization

Ar gas at a pressure of 0.1 MPa was introduced into the microplasma generation nozzle through the micro-nebulizer body at the flow rate of 30 sccm and the UHF power of 20 W was supplied to the coil. Under these conditions, the atmospheric-pressure microplasma was ignited by applying the high-voltage (15 kV) for instance to the inserted wire through the metal tube. Then the ethanol or ferrocene/ethanol solution (ratio of Fe to C atoms is 0.01 %) was fed to the microplasma through the nebulizer by applying the gas pressure (0.15 MPa  $\text{N}_2$ ) to the liquid source material. The feed rate of them was about 12  $\mu\text{l}/\text{min}$ . The resultant products were deposited on the glass-epoxy substrate kept at a gap

distance of 100  $\mu\text{m}$  downstream from the tip.

The deposits were characterized with a field emission scanning electron microscope (FE-SEM, Hitachi S-4800), a transmission electron microscope (TEM, JEOL JEM-2010, 200 kV). In order to identify the active species and clarify a process mechanism in the microplasma processing, OES was performed.

#### 4. RESULTS AND DISCUSSIONS

##### 4.1 Ethanol injection

Fig. 3(a) shows the SEM image (top-view) of the deposit resulted from the ethanol injection for 1 sec. The deposited material was black color and it is on a localized region of about 50  $\mu\text{m}$  diameter. Magnified SEM observation (Fig. 3(b)) indicates that the deposit is composed of the nano-grains. The detailed characterization by TEM indicates that most of the grains with a diameter of 13 – 25 nm are in spherical shape, as seen in Fig. 4(a). A high-resolution TEM observation (Fig. 4(b)) clearly reveals that each grain is composed of the concentric graphitic shells called as carbon nano-onion (CNO).

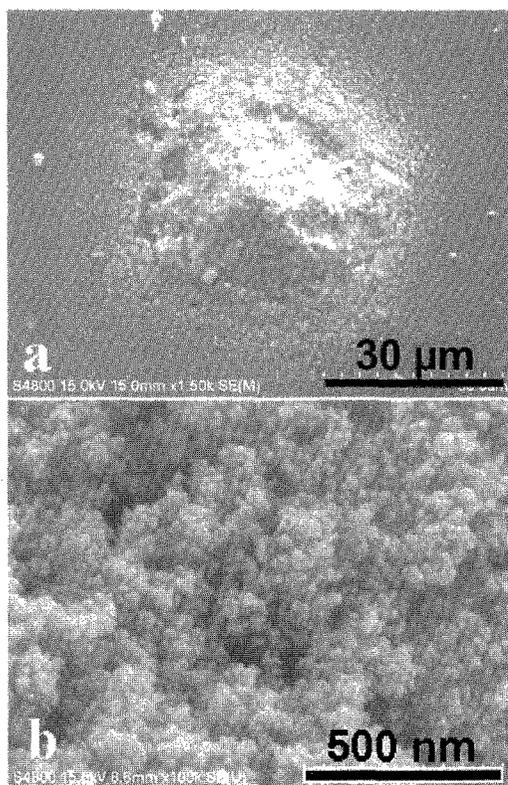


Fig. 3 (a) Top view of the deposit resulted from ethanol (by SEM). (b) Magnified SEM image of the deposit, revealing the deposit is composed of nano-grains.

The careful observation made by TEM shows that the dominant products are the aggregates of the CNOs, and there are some by-products which can be rarely observed on the form of graphite-sheet, amorphous

carbon, and polyhedral shape carbon. To compare this result with another result, CVD was performed by supplying of  $\text{CH}_4$  gas. In this case, the mixtures of amorphous carbon and polyhedral carbon were dominantly formed. Accordingly, the selective formation of the onion-like carbon comes from the ethanol source.

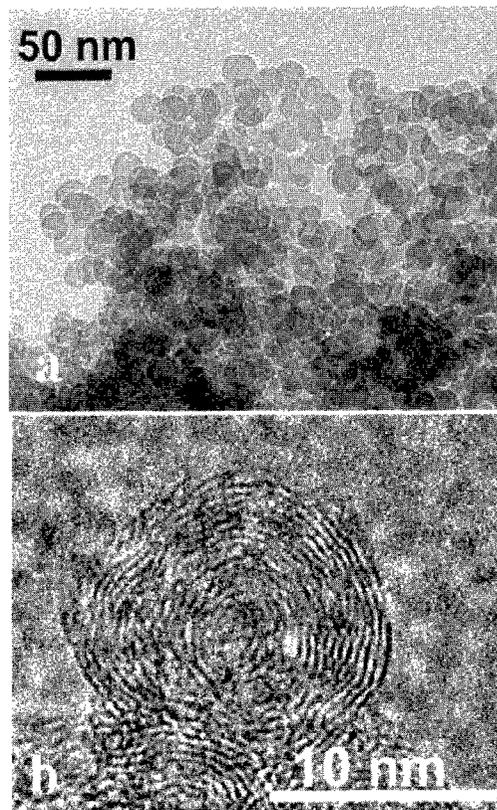


Fig.4 (a) Low-magnification TEM image of the nano-grains as in Fig. 3 (b). (b) High-resolution TEM image of the nano-grain, which composed of concentric graphitic-shells (carbon nano-onion)

The OES measurement indicates the selective formation of the CNOs from ethanol. Fig. 5 shows the emission spectra taken from the point indicated in Fig. 2. The bands of OH (3064 Å system; 282.9 and 308.9 nm), CO (angstrom system; 451.1, 483.5, 519.8, 561.0, 607.9 nm), CH (4300 Å system; 431.4 nm), and  $\text{C}_2$  (swan system; 516.5 nm) appeared, respectively. The appearance of OH and CO bands explains the selective formation of the CNOs, because it is proposed that OH radicals attack nearby carbon atoms with dangling bonds to form CO, and thus seeds of amorphous carbon are efficiently removed in the growth process [9]. In this process, the decomposition of ethanol makes the generation of OH radicals, which could play a similar role as previous, and moreover the CNOs were formed by the condensation of  $\text{C}_2$  radicals, which are typical precursors of carbon material composed of  $sp^2$  bonding [10]. In the spectra, some additional bands such as  $\text{N}_2$

(second positive system; 293.5, 296.2, 315.9 nm) and  $N_2^+$  (first negative system; 358.2 nm) bands are appeared. These bands were detected in the OES from Ar microplasma even without ethanol supplying using the same setup. These bands might be come from the residual air in the nebulizer system. CN (violet system; 386.2 ~ 388.3 nm, 416.8 ~ 421.6 nm) could come from the reactant of the  $N_2$  and ethanol.

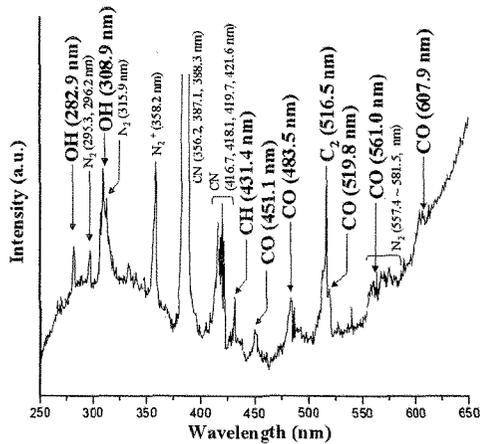


Fig.5 Optical emission spectra of the atmospheric-pressure microplasma after ethanol injection for deposition of the CNOs.

#### 4.2 Ferrocene/ethanol solution injection

By feeding ferrocene/ethanol solution, the SEM observation of the deposit indicates that the nano-grains formed dominantly, are similar as in Fig. 3 (b). However, a careful observation (Fig. 6 (a)) indicates that the tangles of fibrous substances are formed. TEM observation shows that most of the deposit are CNOs and some of them are the tangles of CNTs as shown in Fig. 4(b), which corresponds to fibrous substance as observed in SEM. Typical high-resolution TEM image is shown in the inset of Fig. 6 (b). The obtained CNTs are composed of 3 - 7 layers and with a diameter of 6 - 10 nm. These kinds of CNTs could be formed due to the catalytic effect of Fe in solution, because CNTs were never formed from pure ethanol. In general, CNTs formed through catalytic growth mechanism have the catalytic particle at the ends. However, the TEM results show that no catalytic particle is found at the ends of the CNTs. In future, many more studies will be carried out to solve the relation between Fe and the CNT formation in this process, and these observations may lead to prepare CNTs with high yield and to deposit on localized area directly.

#### 5. ACKNOWLEDGEMENT

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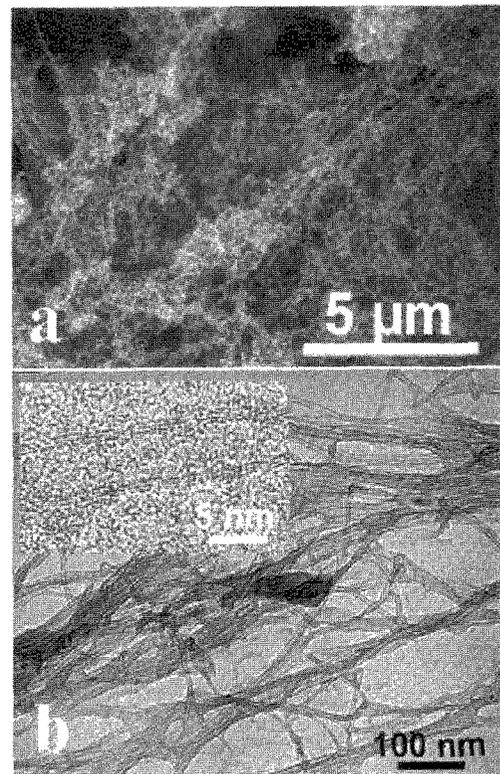


Fig.6 (a) SEM image of the deposits resulted from ferrocene/ethanol solution. Fibrous substances are formed. (b) TEM images of the fibrous substances, which clearly reveals that the fibrous substances are carbon nanotubes.

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