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Carbon-Nanotube Growth in Alcohol-Vapor Plasma

Yoshiyuki Suda, Atsushi Okita, Junichi Takayama, Akinori Oda, Hirotake Sugawara, Yosuke Sakai, Shinichiro Oke, and Hirofumi Takikawa, *Member, IEEE*

***Abstract*—We have successfully grown carbon nanotubes (CNTs) by plasma-enhanced chemical vapor deposition (PECVD) using alcohol. When 0.01-wt% ferrocene was added to the alcohol, vertically aligned CNTs grew at 650 °C. By contrast, a few CNTs and mostly carbon nanoparticles were obtained by pure alcohol PECVD even though the Fe catalyst was coated on Si substrates. Comparing this PECVD experiment with thermal alcohol CVD showed that only the PECVD method can be used to grow CNTs under the reported experimental conditions. To understand the plasma properties for CNT growth, particularly plasma species contained in a gas phase of alcohol plasma, the plasma was analyzed using optical-emission spectroscopy (OES) and quadrupole mass spectrometry (QMS). From the OES measurement, emission peaks from the excitation states of C_2, CH, CHO, CH_2O, CO, H, O_2, C^+, and CO^+ were identified, while the QMS measurement also showed the existence of H_2, O, and CO. These results indicate that, in alcohol plasma, oxidants and reductants exist together and potentially promote/suppress CNT growth depending on the process conditions. The contribution of C_xH_y $(x \geq 1, y \geq 3)$ radicals, which were produced by decomposition reactions in alcohol plasma as a CNT precursor, is discussed.**

***Index Terms*—Carbon nanotube (CNT), ferrocene, mass spectrometry, optical-emission spectroscopy (OES), plasma-enhanced chemical vapor deposition (PECVD).**

I. Introduction

CARBON nanotubes (CNTs) have attracted significant interest due to their unique properties, e.g., high chemical stability, mechanical strength, and current density. Based on these properties, our group has focused on the application of CNTs as nanoscale interconnections in large-scale integrated (LSI) circuits [1], [2]. Plasma-enhanced chemical vapor deposition (PECVD) is superior to other techniques including arc discharge, laser ablation, and CVD for the low-temperature operation of CNT growth ($\sim$390 °C). The PECVD approach meets the condition for the LSI fabrication process ($\leq$ 400 °C) [3]. By contrast, recent reports of CVD growth using O_2 gas [4] and water vapor [5] as an additive to CH_4 and C_2H_4, respectively, provide an enormous advantage in long CNT growth with high yields. These oxidants are thought to play a role in activating catalyst particles for long lifetimes and, thereby, allowing the growth of longer CNTs. Alcohol is also well known to grow high-purity CNTs; Maruyama *et al.* [6] discussed the role of decomposed OH radicals from alcohol for the efficient removal of amorphous carbon during CNT growth.

Our group has studied the PECVD of CNTs using CH_4/H_2 gas mixtures and the correlation among reactions in the plasma gas phase, the state of the catalyst nanoparticles, and the CNT growth conditions [7]–[10]. We have developed a CH_4/H_2 simulation code and have paid close attention to the supply of a carbon source as a precursor for CNTs. To simulate the CNT-growth process, surface chemistry including surface activation and chemical sputtering are necessary [11]. By considering the sticking probabilities of ions and radicals, we estimated the total amount of carbon atoms supplied from the plasma onto the catalyst surface. In our analysis, it was concluded that the $C_2H_5^+$ ion and neutral species $(C_xH_y; x, y > 2)$ are the main precursors for CNT growth [7], [8], [10].

In this paper, we report the use of a new carbon source, alcohol (C_2H_5OH), in PECVD for CNT growth and the analysis of the source's plasma. In this plasma, CNTs can be grown under limited conditions (pressure = 133 Pa, input power = 200 W, temperature = 650 °C, Fe catalysts with Al_2O_3 supports). PECVD of CNTs using C_2H_5OH has been reported [12], [13], but various species, including hydrocarbon radicals, ions, oxidants, and reductants, are present in C_2H_5OH plasma, and the properties of these species remain unclear. Clearly, it is important to understand the characteristics of the plasma species in C_2H_5OH plasma and to investigate the contribution of these species to CNT growth. In this paper, we measured the plasma optical emissions by optical-emission spectroscopy (OES) and investigated the existence of plasma species by quadrupole mass spectrometry (QMS). The C_2H_5OH plasma species monitored by OES and QMS is presented.

II. Experimental Setup

Fig. 1 shows the experimental setup for alcohol PECVD. The details of the experimental setup and CNT growth procedure are described in earlier reports [7]–[9]. The ribbon heater was equipped to provide a stable alcohol-vapor feed. To compare CNT growth, pure C_2H_5OH and C_2H_5OH containing 0.01-wt% ferrocene $(C_{10}H_{10}Fe)$ were used. We prepared the catalyst/support materials on a Si substrate using the electron-beam (EB)-evaporation approach. The substrates used were Si

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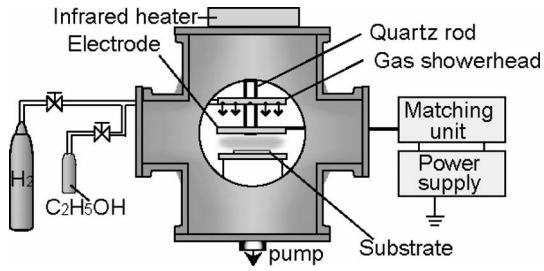


Fig. 1. Experimental apparatus for alcohol plasma-enhanced CVD.

TABLE I
EXPERIMENTAL CONDITIONS

	Pretreatment condition	Process condition
Gas	H_2 (Gas flow rate = 50 sccm)	C_2H_5OH vapor (+ 0.01-wt% Ferrocene)
Pressure	666 Pa	133 Pa
Process temperature	550 °C	650 °C
RF input power	50 W	200 W
Process time	4 min	10 min

wafers with a 20-nm-thick SiO_2 layer. In the EB evaporation, the Fe (catalyst) and Al_2O_3 (support) were deposited on the substrates to form sandwichlike structures $(Al_2O_3/Fe/Al_2O_3 = 1/1/1$ nm), which can then form small nanoparticles [9], [14]. The pretreatment and growth conditions including pressure, power, process temperature, and process time are listed in Table I.

The procedure of CNT growth is briefly described. First, substrates with catalyst and support materials were set on the center of the grounded electrode. The reactor was pumped down to below 10^{-4} Pa. Using an infrared heater, the substrates were heated and kept at 550 °C in 666-Pa H_2 plasma for 4 min. The H_2 gas was removed, and C_2H_5OH (water content $\leq 0.2\%$, with/without 0.01-wt% ferrocene) was introduced. The pressure was maintained at 133 Pa, while the temperature was maintained at 650 °C for 10 min. During CNT growth by PECVD, plasma optical-emission spectra were acquired using a photonic multichannel analyzer (PMA: Hamamatsu Photonics K.K., PMA-11) in the wavelength range of 300–800 nm. A quadrupole mass spectrometer (QMS: ANELVA, M-QA200TS) was used to analyze the plasma species. The QMS tube was connected with the PECVD chamber through a 50-cm-long 1/8-in-diameter stainless-steel pipe and a variable leak valve. Pressure inside the QMS tube was carefully controlled by the valve, and the QMS spectra of CH_4/H_2 gas with/without plasma were evaluated. The CNTs obtained were characterized using a scanning electron microscope (SEM: Hitachi High-Technologies Corporation, S-4800) and a transmission electron microscope (TEM: JEOL, 2000FX).

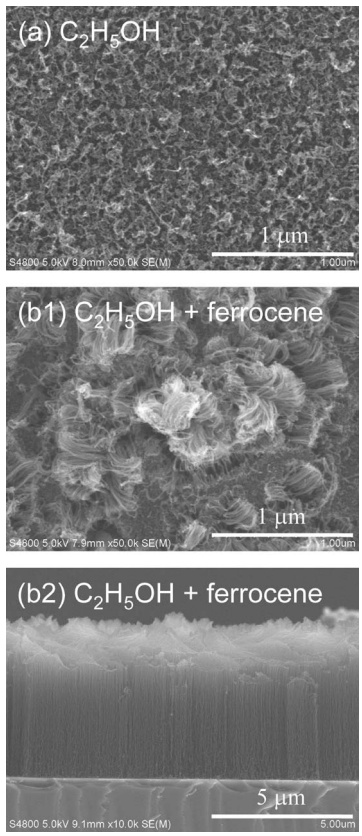


Fig. 2. SEM micrographs of CNTs obtained using a 133-Pa C_2H_5OH plasma. $Al_2O_3/Fe/Al_2O_3$ [$= 1/1/1$ nm, (a), and (b)] is used for the catalyst/support materials. Ferrocene is mixed with C_2H_5OH, and the growth results are shown in (b). (b2) is the cross-sectional view of (b1), which confirms the formation of vertically aligned CNTs.

III. RESULTS AND DISCUSSION

Fig. 2 shows the CNT growth results obtained using C_2H_5OH plasma. The substrate with $Al_2O_3/Fe/Al_2O_3$ showed CNT growth over the whole substrate area, resulting in a high production yield of CNTs. The effect of adding ferrocene can be clearly seen. As shown in Fig. 2(b2), vertically aligned CNTs were obtained when ferrocene was added, although Fig. 2(b1) and (b2) revealed that CNT growth occurred over the whole substrate area. To confirm the effect of the $Al_2O_3/Fe/Al_2O_3$ catalysts, we observed the CNT deposition on a Si substrate. Without catalyst, no CNTs were obtained on a Si substrate even though ferrocene was supplied with the alcohol. This clearly indicated that a carbon source containing a ferrocene molecule can be activated on the catalyst surface and used to grow CNTs. Eres *et al.* [15] used a substrate that was catalyzed using a Mo/Fe/Al multilayer and found that the introduction of ferrocene into the acetylene-gas stream enhanced the growth of vertically aligned CNTs. In addition, CNT growth has been achieved using ferrocene-containing ethanol solutions in spray pyrolysis [12] and inductively coupled plasma [13] techniques. However, the concentrations of ferrocene in these reports (i.e., 1000 mg/100–800 mL by Su *et al.* [12] and 5 mg/10 mL by Xu *et al.* [13]) are higher than the levels used in our experiment (8 mg/100 mL). TEM analysis showed the effect of the addition of ferrocene (Fig. 3). In the absence of ferrocene, a large

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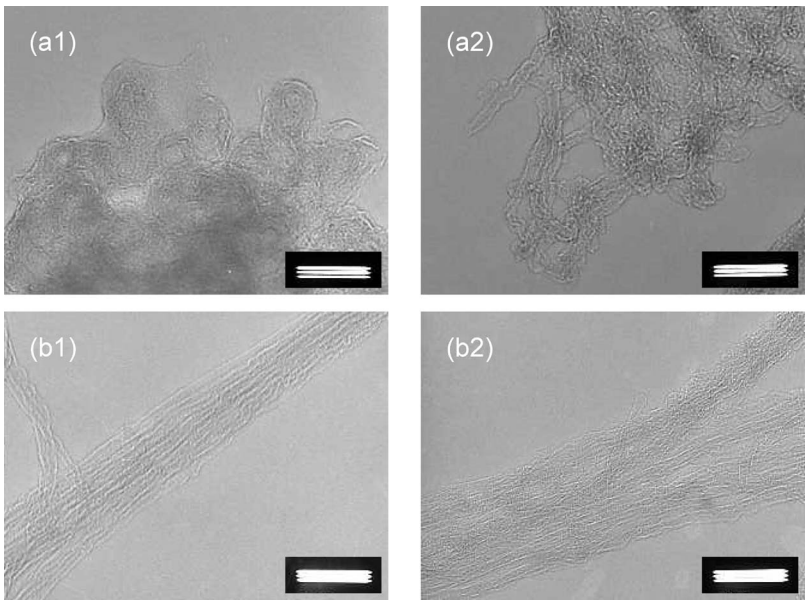


Fig. 3. TEM micrographs of carbon deposits grown from (a) C_2H_5OH only and (b) C_2H_5OH with ferrocene. Scale bar = 50 nm.

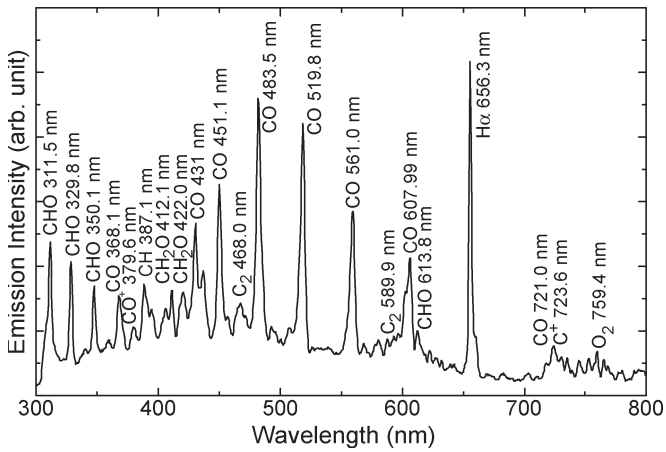


Fig. 4. Optical-emission spectra of C_2H_5OH plasma at 133 Pa.

number of carbon nanoparticles and nanocapsules were formed on the $Al_2O_3/Fe/Al_2O_3$-catalyzed substrate. By contrast, a bundle structure composed of CNTs with a diameter of ∼5 nm was formed by the ferrocene-assisted reaction.

To ensure the effect of plasma, we confirmed that no CNTs were obtained at a substrate temperature of 650 °C without plasma. Chiashi *et al.* [16] who performed single-walled CNT (SWCNT) growth in a cold-wall CVD reported that the effective reaction temperature of alcohol CVD was estimated to be slightly higher than 850 °C, whereas a low-temperature reaction caused the generation of amorphous carbon.

Fig. 4 shows the OES spectra obtained using a 133-Pa C_2H_5OH plasma. The measurements were performed at room temperature to avoid the detection of light from the heating system. As a result of this OES measurement, optical peaks from C_2, CH, CHO, CH_2O, CO, H_α (H atom in the Balmer series), O_2, C^+, and CO^+ were identified. Fig. 5(a) shows the QMS result obtained using a 133-Pa C_2H_5OH plasma. From the QMS analysis, peaks corresponding to each molecular weight were observed: H_2 (between 1 and 3), CH_4 (between 12 and 18), CH_3OH (between 24 and 31), and C_2H_5OH (between 38 and 46). Since the ionization process of particles by electron collision is absolutely necessary for QMS detection, the decomposition of the C_2H_5OH molecule occurs. We measured the QMS peaks obtained in the 133-Pa C_2H_5OH atmosphere [without plasma, Fig. 5(b)]. Fig. 5(c) shows the subtraction of the spectral intensity of plasma-off [Fig. 5(b)] from that of plasma-on [Fig. 5(a)]. The result indicates that the peaks of C_2H_5OH-derived molecules (CH_4, CH_3OH, and C_2H_5OH) decreased by igniting the plasma. This shows that the decomposition of C_2H_5OH is promoted by generating plasma. By contrast, the species of H_2, O, CO, and C_2H_4 (atomic/molecular weight = 2, 16, 28, and 28, respectively) increased by the recombination/dissociation processes. These results reflect the observation that plasma processes can promote the production of several species by plasma reactions.

In this paper, we discuss the decomposition/dissociation reactions of C_2H_5OH plasma. Several groups [17]–[21] have reported the chemical-reaction processes of C_2H_5OH plasma.

$$C_2H_5OH \rightarrow C + CO + 3H_2 \quad (1)$$

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \quad (2)$$

$$C_2H_5OH + H_2O \rightarrow 2CO + 4H_2 \quad (3)$$

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \quad (4)$$

$$C_2H_5OH \rightarrow C_2H_5 + OH. \quad (5)$$

Reaction (1) is a collision-impact process between electrons and radicals in plasma [17] as well as a typical reaction occurring on a catalyst surface for CNTs growth by nonplasma alcohol CVD. However, the CNT formation in this experiment could not be explained simply by this reaction, since no carbon

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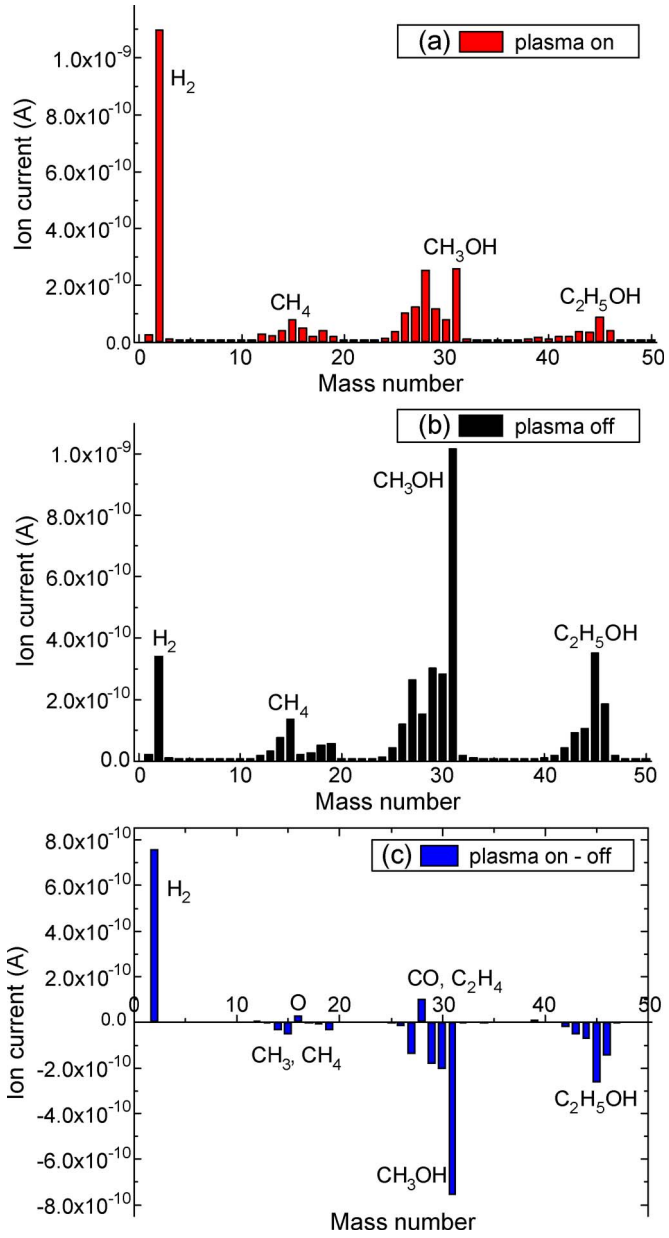


Fig. 5. Mass spectra obtained by (a) C_2H_5OH PECVD and (b) C_2H_5OH vapor (without plasma) at 133 Pa. (c) Subtraction of (b) from (a).

deposit was observed without plasma. Generation of CO, CO_2, and H_2 as proposed by reactions (1)–(5) is consistent with the presented OES and QMS analyses. A small amount of H_2O ($\leq 0.2\%$) was present in the ethanol used, and therefore, reactions (2) and (3) take place. Considering the dissociation energies by electron collision of CO, CO_2, OH, H_2, and H_2O, namely, 11.09, 5.2, 4.39, 8.8, and 7.0 eV, respectively [17], [22]–[25], it was observed that these species were easily dissociated in the plasma and possibly adsorb onto the catalyst surface. This could explain the requirement of ferrocene for CNT growth.

CO_2, H_2O, and OH, which work as oxidants, and CO and H_2, which operate as reductants, are simultaneously produced in the gas phase through reactions (1)–(5). Several papers describe their effects on CNT growth, e.g., supergrowth of SWCNTs by the addition of a small amount of H_2O (175 ppm) in the carbon source (C_2H_4) [5], the oxidation of the catalyst by existing OH radicals [6], and the optimization of the carbon/hydrogen ratio by O atoms [4]. Among the aforementioned molecules (CO_2, H_2O, OH, CO, and H_2), only CO can be used as a carbon source for CNT by a CO disproportionation reaction below 900 °C [26]. These species produced in the plasma have a strong influence on the catalyst state and CNT growth by varying their concentration in the gas phase.

A recent experiment by Oshima *et al.* [27] showed that C_2H_5OH thermally decomposed at 840 °C without plasma and a metal catalyst, and C_2H_4, C_2H_2, C_2H_4O, CH_4, CO, CO_2, and H_2O were generated through the thermal reactions. This paper suggested that hydrocarbons such as C_2H_4 and C_2H_2 can be used as a CNT precursor. Our previous work using CH_4/H_2 plasma concluded that $C_2H_5^+$ and C_xH_y $(x, y \geq 2)$ are the main precursors [7], [8], [10] and that $Al_2O_3/Fe/Al_2O_3$ catalyst resulted in high yields of CNTs. According to the present QMS measurement, the radicals derived from the C_2H_5OH molecule are the major species in the plasma. The species observed by QMS are different from those by OES because the emission peaks of hydrocarbon radicals are located in the infrared region and outside the measurement range. Considering these results, we speculate that C_2H_4 and C_2H_5 which were generated by electron impact collision with C_2H_5OH would be CNT precursors in this system. Since the molecular weight of CO and C_2H_4 are equivalent, it is difficult to distinguish between these two species [Fig. 5(c)]. The presence of CO indicates that carbon is provided by the CO disproportionation reaction [26]. By employing plasma, the electron-collision process in the plasma reduces the effective temperature for CNT growth by approximately 200 °C, when compared with the nonplasma CVD process [27].

IV. Conclusion

In this paper, we reported multiwalled CNT growth by alcohol PECVD at 650 °C. By adding 0.01-wt% ferrocene in C_2H_5OH, the yield of CNTs increased, and well-aligned CNTs were grown on an $Al_2O_3/Fe/Al_2O_3$ substrate. Using plasma OES, the spectral peaks from the resulting atoms and molecules (C_2, CH, CHO, CH_2O, CO, H, O_2, C^+, and CO^+) were identified. In the QMS measurement, the peaks of H_2, CH_4, CH_3OH, and C_2H_5OH were detected, and a decrease in intensity of CH_4, CH_3OH, and C_2H_5OH by generating plasma was shown. By utilizing the plasma dissociation process for alcohol, oxidants (such as CO_2, H_2O, OH) and reductants (CO, H_2), as well as C_xH_y $(x \geq 1, y \geq 3)$ that are precursors for CNT growth, can be effectively produced at a lower temperature in plasma.

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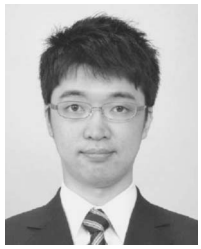
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