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 (≤ 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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Y. Suda was with the Graduate School of Information Science and Technology, Hokkaido University, Sapporo 060-0814, Japan. He is now with the Department of Electrical and Electronic Engineering, Toyohashi University of Technology, Toyohashi 441-8580, Japan (e-mail: suda@eee.tut.ac.jp).

A. Okita was with the Graduate School of Information Science and Technology, Hokkaido University, Sapporo 060-0814, Japan. He is now with Hitachi High-Technologies Corporation, Hitachinaka 312-8504, Japan.

J. Takayama, H. Sugawara, and Y. Sakai are with the Graduate School of Information Science and Technology, Hokkaido University, Sapporo 060-0814, Japan.

A. Oda is with the Department of Engineering Physics, Electronics and Mechanics, Graduate School of Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan.

S. Oke and H. Takikawa are with the Department of Electrical and Electronic Engineering, Toyohashi University of Technology, Toyohashi 441-8580, Japan.

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