Available online at www.sciencedirect.com
ScienceDirect
Thin Solid Films 516 (2007) 277–283
www.elsevier.com/locate/tsf

Influence of CO_2 and N_2 on the growth of carbon nanotubes by using thermal chemical vapor deposition

Mi Chen [a,*], Yu-Cheng Kao [b], Hung-Wei Yu [b], Su-Chen Lu [b], Horng-Show Koo [c]

[a] Department of Materials Science and Engineering, Minghsin University of Science and Technology Hsinfeng, Hsinchu 304, Taiwan, ROC
[b] Department of Chemical Engineering, Minghsin University of Science and Technology Hsinfeng, Hsinchu 304, Taiwan, ROC
[c] Department of Optoelectronics System Engineering, Minghsin University of Science and Technology Hsinfeng, Hsinchu 304, Taiwan, ROC

Available online 14 August 2007

Abstract

Carbon nanotubes (CNTs) have been grown efficiently on a Si substrate by thermal chemical vapor deposition using CH_4 and CO_2 gas mixtures. Fe catalytic nanoparticles were deposited on Si and carbon cloth substrates. This process is apparently different from the conventional process in gas mixtures of H_2/CH_4, H_2/C_2H_2, NH_3/CH_4, H_2/C_6H_6 and others. Carbon dioxide is used to replace the harmful gases of H_2 and NH_3 and the addition of N_2 in the mixture gas of CH_4 and CO_2 obviously improves the growth and quality of CNTs, and allows study of the reaction growth of CNTs. This paper demonstrates the effects of compositional ratio of CH_4, CO_2 and N_2 in the mixture gas on the growth of carbon nanotubes under atmospheric conditions. Various substrates of Si and carbon cloth were used to synthesize CNTs by using CH_4–CO_2–N_2 gas sources. A significant difference in morphological structure was observed and analyzed on the different substrates of Si and carbon cloth. By proper adjustment of growth parameters, high quality CNTs were observed on Fe-deposited substrates. The characteristics of the as-grown carbon nanotubes on different substrates were analyzed by SEM, TEM and Raman spectroscopy.

Keywords: Carbon nanatubes; Thermal chemical vapor deposition; Reaction growth; Carbon cloth; Catalytic nanoparticles; Raman spectroscopy

1. Introduction

Since carbon nanotubes (CNTs) were discovered [1], research and development of commercial applications has progressed rapidly. Many synthesis techniques have been developed [2–7]. Thermal chemical vapor deposition has been regarded as a potential method of mass production because carbon nanotubes can grow over large-areas, on irregular-shaped substrates and with simple equipment at low cost at atmospheric pressure. In recent years, a number of research groups have investigated and characterized CNTs growth and have worked to improve the process of thermal chemical vapor deposition. Lee and coworkers have studied the effect of catalysis such as Fe, Co, and Ni on CNTs synthesized by thermal chemical vapor deposition of acetylene gas at 750~950 °C[8]. Moshkalyov et al. have investigated the effect of different gases used for the catalyst surface pretreatment (N_2, H_2, or NH_3). Higher density of nucleation and growth was obtained using hydrogen and ammonia [9]. Chio et. al reported that effects of ammonia on the alignment of CNTs in Ni-assisted thermal chemical vapor deposition at 800~900 °C [10]. They emphasized that synthesis by C_2H_2 after ammonia pretreatment and synthesis by NH_3/C_2H_2 gas mixture both promoted vertical alignment of CNTs. Juang et al. claimed that the role of ammonia was considered to enhance the catalyst activity by preventing passivation [11]. Lee et al. investigated growth and field emission of carbon nanotubes on sodalime glass at 550°C using thermal chemical vapor deposition [12]. Lee et al. reported that diameter and growth rate of vertically aligned CNTs are controlled by modulating the size of catalytic particles using thermal chemical vapor deposition [13]. The size of Fe catalytic particles deposited on silicon oxide substrates was varied in a controlled manner by adjusting the condition of ammonia pretreatment.

The role of ammonia on growth of good quality, vertically aligned MWCNTs in the thermal chemical vapor deposition method has been widely studied. It was generally agreed that ammonia gas helps to maintain metal catalyst surface activity by

* Corresponding author. Tel.: +886 3 5593142x3339; fax: +886 3 6007577.
E-mail address: chenmi@must.edu.twd (M. Chen).

0040-6090/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2007.07.211

reacting with amorphous carbon [14–16]. Juang et al. suggested that there exists a critical supply of CH_4 or other carbon source when CNTs growth [17]. Liu et al. have reported this effect of excess carbon content in Fe catalyst coatings in the growth of vertically aligned CNTs on smooth silicon surfaces by thermal chemical vapor deposition [18].

In our previous studies, microwave plasma chemical vapor deposition was successfully used to synthesize multi-walled carbon nanotubes with a carbon dioxide and methane gas mixture [19]. We found that by substituting carbon dioxide for hydrogen in CH_4–CO_2 gas mixture, a high yield of vertically aligned multi-walled carbon nanotubes could be synthesized at low temperature [20].

In the present work, carbon nanotubes were grown on catalytic nanoparticles deposited on a Si substrate and carbon cloth by thermal chemical vapor deposition using CH_4 and CO_2 gas mixtures. This is apparently different from the conventional reaction in gas mixtures of H_2/CH_4, H_2/C_2H_2, NH_3/CH_4, H_2/C_6H_6 and so on. Carbon dioxide is used to replace the harmful gases of H_2 and NH_3. The addition of N_2 in the mixture of CH_4 and CO_2 obviously improves the growth and quality of CNTs. The influence of addition of oxygen and nitrogen gas sources and temperature on the growth of CNTs are investigated. Various substrates of Si and carbon cloth were used to synthesize CNTs by using CH_4–CO_2–N_2 gas sources. An atomic C–H–O CNTs deposition phase diagram with the graphite domain have been investigated and compared with Bachmann model.

The crystallinity and microstructure of CNTs grown on Fe-deposited substrate were investigated using scanning electron microscopic (SEM), high resolution transmission electron microscopic (HRTEM), and Raman spectroscopy.

2. Experimental

The Fe catalyst nanoparticles were deposited on n-type Si (100) wafers by sputtering and deposited on carbon cloth by e-beam evaporation. The thickness of the catalyst was 10 nm. The experiments were carried out in a thermal chemical vapor deposition reactor. Fig. 1 shows a thermal chemical vapor deposition chamber. The 20×20 mm deposited metal-catalyst substrate was placed in a quartz wafer boat. When the sample boat was placed in the zone of the process tube, the temperature started to ramp up with argon gas flowing. The ramp rate was set at about 10 °C/min. The argon was used as an inert idle gas with the flow rate of 200 sccm. After the furnace temperature reached the setting temperature, the gas flows of CO_2, CH_4 and N_2 were started and the Ar flow was turned off. The gases reacted and carbon nanotubes were deposited on the substrate. After the required carbon nanotubes thickness was reached, the CO_2 and CH_4 gas flow were terminated and Ar flow was resumed. The experimental conditions are summarized in Table 1.

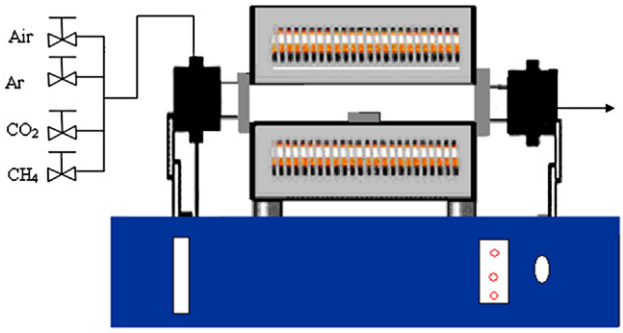

Fig. 1. Schematic of thermal chemical vapor deposition multi-walled carbon nanotubes synthesis apparatus.

Table 1
Experiment condition

Substrate	n-Si (100), carbon cloth
Ar flow rate	100 sccm
Temperature	700~900 °C
Reaction time	5, 10, 15, 20 min
Flow rate of CH_4	0~100 sccm
Flow rate of CO_2	0~100 sccm

After deposition, a scanning electron microscope (Jeol-6700) was used to examine the morphology of the carbon nanotubes. A high resolution transmission electron microscope (Philips Tecnai-20) was then used to investigate the microstructure of the CNTs. The CNTs were characterized by a Raman spectrometer (Renishaw system 200), driven with an argon-ion laser at a wavelength of 514.5 nm.

3. Results and discussion

3.1. The effects of N_2 and CO_2 in the gas mixture on CNTs growth

Fig. 2 shows the SEM images of CNTs with various CO_2/CH_4/N_2 flow ratios at 890 °C. The deposition time was 12 min for each case. Fig. 2(A) shows that for CO_2/CH_4 flow rates of 100 sccm/100 sccm, only rarely are CNTs formed, those that do appear are not uniform in size, and mostly amorphous carbon appeared on the substrate. We have suggested that excess carbon atoms tend to form amorphous carbon and CNT growth is hindered due to catalyst passivation. Decreasing the flow of reactants with the same ratio of CO_2/CH_4 to 50 sccm/50 sccm, produced films as shown in the SEM image of Fig. 2(B). The quality of CNTs is better than that for the higher flow rates but irregular CNTs and amorphous carbon are still found. The SEM image of CNTS synthesized in $CO_2/CH_4/N_2$ with 50 sccm/50/sccm/10 sccm flow rate is shown in Fig. 2(C.). There is apparently an improvement in CNT deposition due to the addition of small amount of nitrogen to the CH_4–CO_2 gas mixture. Fig. 2(D) shows high quality CNTs grown at CO_2/CH_4/N_2 with 50 sccm/30 sccm/20 sccm flow rate. This sequence shows how the relative variation of the CO_2–CH_4–N_2 ratio affects the growth condition of CNTs . Carbon dioxide has been used to replace the harmful gases of H_2 and NH_3 and the addition of N_2 in the mixture gas of CH_4 and CO_2 obviously improves the growth and quality of CNTs. We suggest that in the CO_2–CH_4–N_2 gas mixture, the reaction mechanism follows these equations:

$$CH_{4(g)} + CO_{2(g)} \leftrightarrows 2CO_{(g)} + 2H_{2(g)} \quad (1)$$