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GROWTH OF VERTICALLY ALIGNED SINGLE-WALLED CARBON NANOTUBES USING ALCOHOL CATALYTIC CVD METHOD

Mohd Asyadi Azam*, M. A. Mohamed, E. Shikoh, and A. Fujiwara

School of Materials Science,
Japan Advanced Institute of Science and Technology,
1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

***(asyadi@jaist.ac.jp)**

ABSTRACT : A massive growth of vertically aligned single-walled carbon nanotubes (SWCNTs) from Al_2O_3-supported Co catalyst was performed using Alcohol Catalytic Chemical Vapor Deposition (ACCVD) method. Carpets of SWCNTs with an almost submillimeter height were grown on the Si/SiO_2 substrates via this technique. Growth temperature dependence analysis had been carried out in the first place to elucidate parametric study in determining optimum growth conditions, in which the CVD time was fixed at t = 10 min and CVD reactor internal pressure at 3 kPa. The analysis confirmed the maximum height of SWCNTs films grown on the substrate to be T_{CVD} = 750 ° C. Structural properties of as-grown SWCNTs have been measured by Raman spectroscopy with various laser excitations where we confirmed a relatively high quality and pure SWCNTs: determined from Raman intensities, I_G/I_D ratio. Morphology observation of the very high SWCNTs yield was performed by Scanning Electron Microscope (SEM).

KEYWORDS : Vertically aligned SWCNTs, ACCVD, CVD temperature dependence, Raman spectra analysis

INTRODUCTION

Due to their seamless structure, small diameter, and to the resilience of individual carbon-carbon bonds, carbon nanotubes (CNTs) have extreme stiffness, strength, and thermal conductivity (http://www.matweb.com & National Academy of Science, 2005) which exceed all other known natural and synthetic materials. Recently, single-walled CNTs (SWCNTs) are intensively studied compared to others because they exhibit important properties that are not shared by other CNTs variants.

Technologies by thermal Chemical Vapor Deposition (CVD) on catalyst-coated substrates, with further emphasis and precise control of CNTs growth are suited toward studying limited aspects of the growth reactions, and developing industrially-scalable manufacturing processes for well-ordered CNTs. Significant advance in SWCNTs research was the growth of vertically aligned (VA) SWCNTs. This had previously known achieved using multi-walled CNTs (MWCNTs), but not for SWCNTs. The massive vertical growth of SWCNTs using ethanol CVD method was first reported in 2004 (Mukarami *et al.*, 2004), with cobalt–molybdenum as catalyst. Later, several groups successfully synthesized well aligned SWCNTs forests with a millimeter height, mainly by water-assisted method (Hata *et al.*, 2004; & Noda *et al.*, 2007).

In optimizing the high-precision SWCNTs growth for the application of CNT-based electronic devices, a direct growth technique was developed particularly using low-cost ethanol vapor gas (Inami *et al.*, 2008; Mohamed *et al.*, 2008; & Mohamed *et al.*, 2010) and metal catalysts thin films. In contrast with the electronic devices, successful fabrication of well organized structures were only demonstrated for MWCNTs; though similar structures could be made from SWCNTs that are much smaller in size and, naturally much more difficult to vertically self-aligned. For example, in SWCNT-based supercapacitors application (Lu *et al.*, 2009), MWCNTs are widely used. However, SWCNTs were reported to have better power densities and specific capacitances to upgrade current CNT-based electrodes performance because they were composed of only one single carbon network layer. In this paper, this work focuses on the effect of CVD temperature analysis on vertically aligned SWCNTs from Al_2O_3-supported Co catalyst. Raman spectroscopy was used as a measurement tool with various laser excitations in order to study SWCNTs grown behavior and their structural changes.

MATERIALS AND METHOD

VA-SWCNTs were grown from Al_2O_3-supported Co catalyst using alcohol catalytic CVD (ACCVD) method. A silicon wafer with a 400 nm-thick thermally oxidized SiO_2 layer on the surface was used as the substrate. Support material, Al (20 nm) and Co (0.5 nm) catalyst thin-films were deposited on the substrate by electron-beam deposition process. For the formation of the support material Al_2O_3, deposited Al films were air-oxidized at room temperature, and baked at 400 °C in air for 10 min just before the growth process. Ar/H_2 (3% H_2) as pre-treatment gas was purged into the reactor at 400 Pa during 4 min heating up process. CVD temperatures (T_{CVD}) were set to 700, 750, 800, 850 and 900 °C for different substrates. As the furnace reached the CVD temperature, the Ar/H_2 gas flow was stopped and ethanol gas with flow rate of 100 - 150 sccm was introduced to the reactor immediately. Internal pressure of the reactor was controlled to 3 kPa, and CVD process time (t) was fixed to 10 min. The SWCNTs were mainly characterized using Raman spectroscopy (Tokyo Instruments; Nanofinder 30), and Scanning Electron Microscopy (SEM; Hitachi S4100).

RESULTS AND DISCUSSION

Figure 1 shows a massive growth of vertically aligned SWCNTs from Al_2O_3-supported Co catalyst. SWCNTs film with an almost 60 μm height was grown on the substrate. CVD growth temperature analysis had been carried out in the first place to elucidate parametric study in determining the optimum growth conditions using our CVD system.

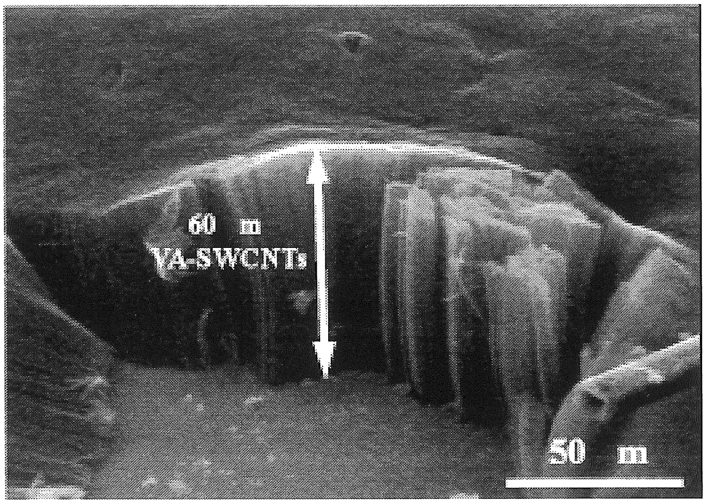

Figure 1. *SEM image of vertically aligned SWCNTs at* T_{CVD} *= 750 °C.*

Figure 2 depicts the Raman spectra measured for the as-grown SWCNTs for all CVD temperatures using 632.8 nm excitation laser. Raman spectra for all samples involve peaks of radial breathing mode (RBM) from 100 to 300 cm^{-1}, which reveal the presence of SWCNTs, D-band around 1310 cm^{-1}, and G-band around 1590 cm^{-1} (Saito *et al.*, 1998; Dresselhaus *et al.*, 2000; & Dresselhaus *et al.*, 2005). From Figure 2, it was found that the SWCNTs growth process was progressing until T_{CVD} = 750 °C. However, at higher temperature, the G-band and RBM peak intensities became weaker. Strongest Raman intensity for RBM region was detected at T_{CVD} = 750 °C. This confirmed the highest yield of SWCNTs (rather than other CNTs variants) were grown compared to other CVD temperatures, and shows an agreement to the film thickness result in Figure 1.

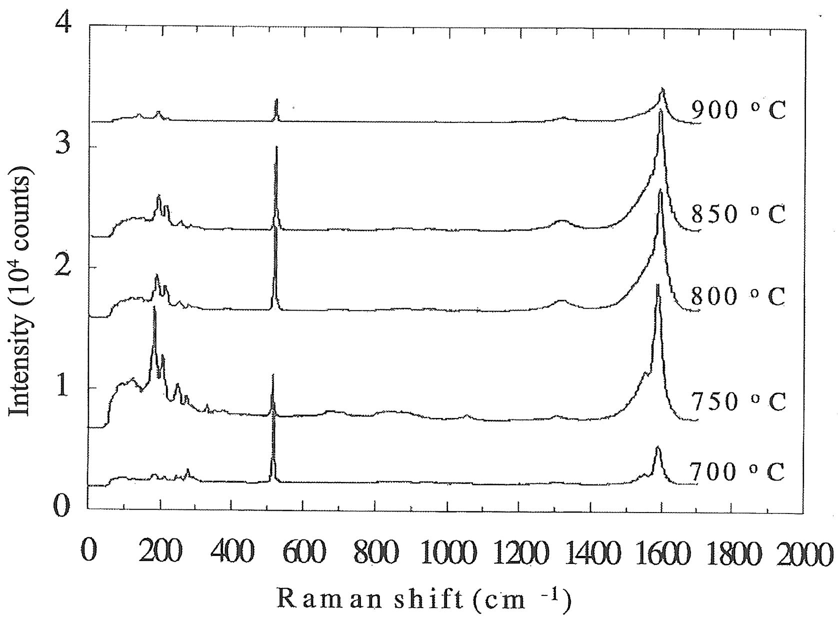

Figure 2. *Raman spectra of as-grown SWCNTs measured by 632.8 nm laser excitations for all CVD temperatures.*

Raman spectra observed in Figure 2 clearly indicated a weak and small D-band intensity for all CVD temperatures: D-band peak originates from the defect, and can be attributed to the CNTs defective by-products and/or the amorphous carbon. G-band and D-band peak intensity ratio, I_G:I_D are shown in Figure 3, which also explains the relation to the grown SWCNTs film thickness. The high I_G:I_D ratio up to 9.5 indicates a relatively good level of purity and quality (Chiu *et al.*, 2006; & Einarsson *et al.*, 2008), especially for those using oxide support layer for the growth process. It should be noted that we characterized the as-grown SWCNTs on substrates without any purification. The I_G/I_D ratio shows an almost similar tendency to the grown SWCNTs film thickness for this analysis. As CVD temperature increased, the purity level and SWCNTs film thickness will decrease in a similar way.

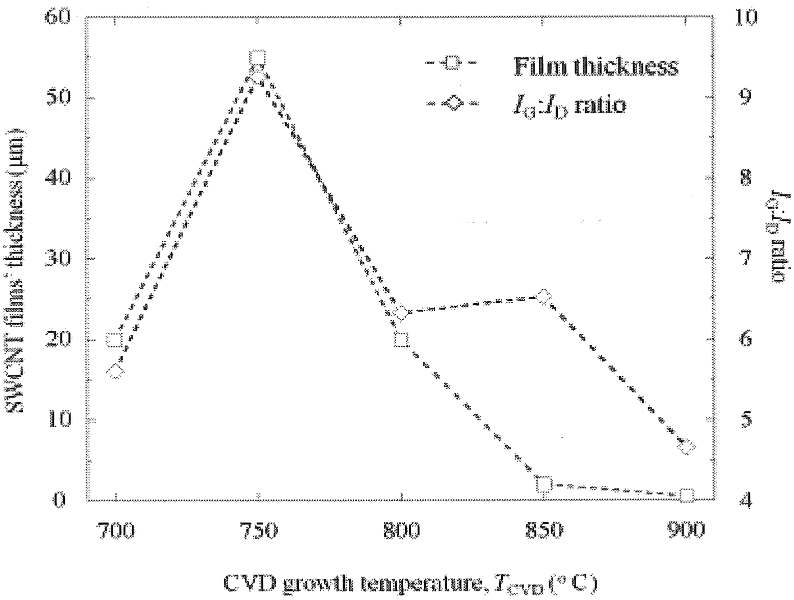

Figure 3. *Relation of CVD growth temperature (T_{CVD}), SWCNTs film thickness, and I_G:I_D ratio.*

The optimum CVD growth temperature, T_{CVD} of VA-SWCNTs was suggested at 750 °C using our CVD technique. As T_{CVD} increased, the experimental results explained the tendency of the decrease of the purity level and SWCNTs film thickness (yield). At present, we proposed that the VA-growth process at higher temperature would elaborate the possibility of Co catalyst poisoning and/or burning out SWCNTs phenomenon (Einarsson *et al.*, 2008; & Mohd Asyadi Azam *et al.*, 2010) which occurred during the growth process.

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