Synthesis of Thin Multiwalled Carbon Nanotubes for Field Emission by Optimizing Gas Compositions in Thermal Chemical Vapor Deposition

Hong Jun Jeon , Hyun Jin Cho, Young Rae Kim, and Naesung Lee
Faculty of Nanotechnology and Advanced Materials Engineering
Sejong University, Seoul 133-791, Korea
TEL: 82-02-3408-3786, e-mail: nslee@sejong.ac.kr

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Abstract

This study investigated the effect of H_2 upon the growth of CNTs by changing the ratios of H_2 to Ar during the growth using C_2H_2. With higher contents of H_2 in Ar, CNTs became longer and thinner, resulting in their higher aspect ratios.

1. Introduction

Although carbon nanotubes (CNTs), first observed by Iijima [1], which are characteristic of unique physical and chemical properties, have drawn much attention as new materials, the growth of high-quality CNTs is prerequisite to their versatile applications. Many methods to synthesize CNTs have been reported including arc discharge [2], laser vaporization [3], pyrolysis [4], and thermal or plasma-enhanced chemical vapor deposition (CVD) [5-6]. Among them, the thermal CVD has been used long in most cases to deposit vertically aligned CNTs over a large area at low temperatures, owing to their simplicity of a system and low cost of operation. For the high-end applications, CNTs are needed to be controlled in terms of diameters, lengths, defects, carbonaceous impurities, etc[7-9]. This study investigated the effects of H_2 gas on the morphologies and crystalline nature of CNTs grown by changing the ratios of H_2 to Ar when using C_2H_2 gas as a feedstock.

2. Experimental

Fig. 1 shows a schematic of thermal CVD system used in this study. CNTs were synthesized on Si substrates which had been deposited with Ti(50 nm)/Al(15 nm)/Invar(2 nm) and Cr(50 nm)/Al(15 nm)/Invar(2 nm). The furnace temperature and pressure were fixed at 650°C and 1.5 torr, respectively. A sample was loaded inside a quartz tube at 650 °C, where Ar was flowed, by a loading bar. Following the annealing for 8 min, the growth of CNTs was carried out for 10 min by switching to the growth gases. During growth, C_2H_2 was used as a feedstock, while Ar and H_2 were used as a carrier gas. A total gas flow rate of Ar, C_2H_2 and H_2 were fixed at 175 sccm. While feeding 25 sccm of C_2H_2, the flow rate of H_2 was changed from 0 to 150 sccm, balanced by Ar. Here, the standard pretreatment and growth conditions are shown in Fig. 2 As-grown CNTs were characterized by using SEM (S-4700, HITACHI), TEM (Tecnai f20, PHILLIPS), and Raman spectroscopy.

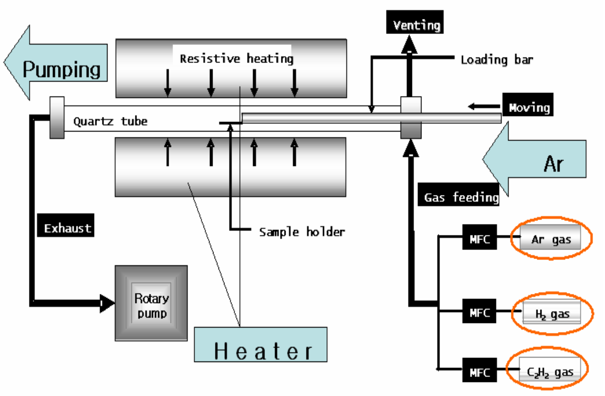


Fig. 1. Schematic of a thermal chemical vapor deposition system used in this study.

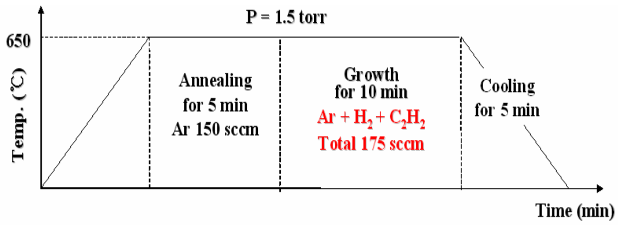


Fig. 2. Temperature profile and gas flows during annealing and growth steps employed for the synthesis of CNTs.

3. Results and discussion

Fig. 3 shows SEM images of CNTs grown at different Ar:H_2 ratios during the growth step, on the Si wafer deposited with Ti(50 nm)/Al(15 nm)/Invar(2 nm). In this case, annealing and growth were performed for 5 and 10 min, respectively. Fig. 4 presents SEM images of CNTs grown at the same condition as that of Fig. 3 but grown on Si wafer deposited Cr(50 nm)/Al(15 nm)/ Invar(2 nm). The diffusion barrier, coated just over the Si wafer, was changed from Ti to Cr for the CNT growth, while the other conditions were kept the same in both cases. The lengths and diameters of CNTs (Fig. 3, 4 : SEM images) grown on two different types of substrates as a function of H_2 flow rates are given in Fig. 5. As increasing the H_2 flow rates, for the Ti diffusion barrier, the length of CNTs are increased up to ~26 μm at 75 sccm H_2, but are saturated at higher flow rates. On the contrary, for the Cr diffusion barrier, CNTs exhibit the largest length of ~20 μm at 75 sccm H_2 and then become shorter at higher flow rates. The change of CNT diameters with the H_2 flow rates exhibits the opposite tendency as that of CNT lengths. The Ti and Cr samples show the smallest CNT diameters of ~7 and ~14 nm, respectively, at 75 sccm H_2.

In our study, Ti seems to be more adequate as a diffusion barrier than Cr, because the longer and thinner CNTs are usually grown in case of the Ti barrier, irrespective of the H_2 flow rates. CNTs grown on the Ti/Al/Invar with different H_2 flow rates were characterized by the intensity ratios of their G and D bands, I_G/I_D, as shown in Fig. 6. The G band of CNTs is attributed to the tangential mode of C-C vibration, while the D band occurs due to lattice defects in the CNTs and carbonaceous impurities such as amorphous carbon. Thus, the I_G/I_D ratio can serve as an indicator of the relative amount of defects and carbonaceous impurities between CNT samples.

The ratio is decreased by adding a small amount of H_2 during growth, but is recovered to the same level at 75 sccm H_2 as that of CNTs grown without H_2 and then show little change at higher flow rates of H_2. The CNTs grown at 75 sccm H_2 (Ar:H_2 = 75 sccm:75 sccm) shows the highest length, the smallest thickness, and the small amount of defects and impurities. Fig. 7 gives high-magnification TEM images of CNTs grown at the Ar:H_2 ratios of 150:0 and 75:75, on the Ti diffusion barrier, which reveals the CNT diameters of ~ 17 and ~7 nm, respectively. The 7-nm-diameter CNT is of triple walls. An addition of H_2

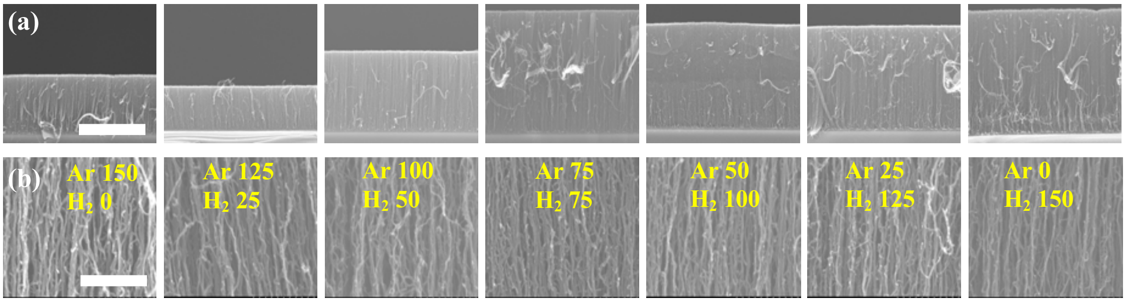


Fig. 3. SEM images of CNTs grown by changing the Ar:H_2 ratio for the fixed flow rate of C_2H_2, on the Si wafer deposited with Ti(50 nm)/Al(15 nm)/Invar(2 nm), to show (a) their heights and (b) diameters. The numbers in (b) correspond to the flow rates of Ar and H_2 gases. Scale bars (a) and (b) indicate 10 μm and 500 nm, respectively.

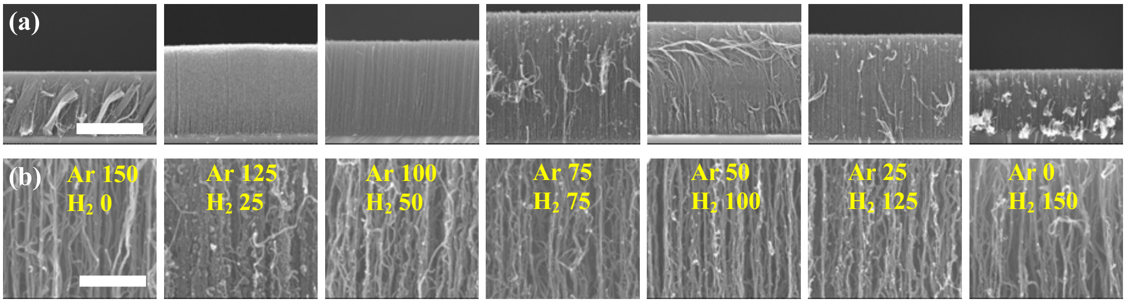


Fig. 4. SEM images of CNTs grown by changing the Ar:H_2 ratio for the fixed flow rate of C_2H_2, on the Si wafer deposited with Cr(50 nm)/Al(15 nm)/Invar(2 nm), to show (a) their heights and (b) diameters. The numbers in (b) correspond to the flow rates of Ar and H_2 gases. Scale bars (a) and (b) indicate 10 μm and 500 nm, respectively.

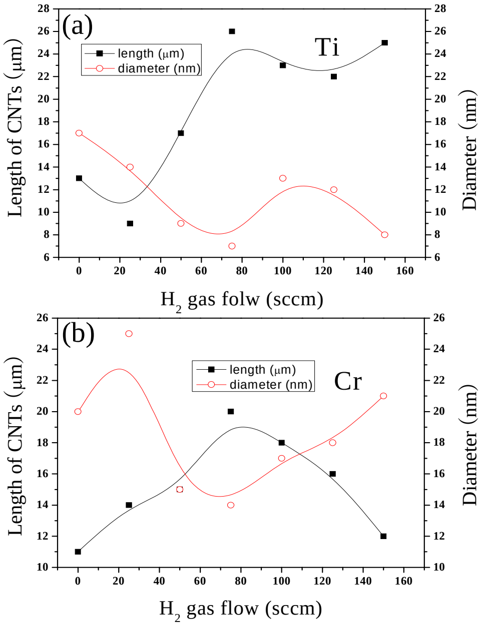


Fig. 5. Lengths and diameters of CNTs (Fig.3, 4 : SEM images) grown with the different flow rates of H_2 on (a) Ti(50 nm)/Al(15 nm)/Invar(2 nm) and (b) Cr(50 nm) /Al(15 nm)/Invar(2 nm).

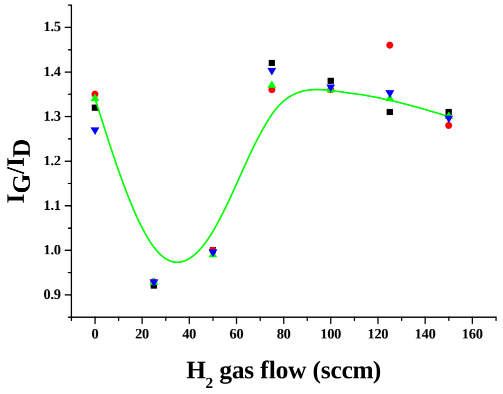
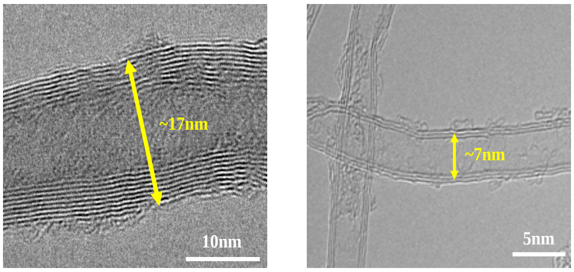


Fig. 6. Intensity ratios of G and D bands, I_G/I_D, of CNTs grown on Ti/Al/Invar with various H_2 flow. The ratios were measured four times for each sample.

seems to considerably decrease the diameters of CNTs and at the same time increase their lengths[10]. It appears that H_2 does not only form smaller catalyst particles by preventing their agglomeration, but also slows down the deactivation rate of catalyst or produces a larger amount of growth precursors during growth.



(a) (b)

Fig. 7. High-resolution TEM images of CNTs grown at the Ar:H_2 ratios of (a) 150:0 (scale bar: 10 nm) and (b) 75:75 (scale bar: 5 nm).

4. Summary

As a diffusion barrier in the CNT growth on Si, Ti seems to be more appropriate than Cr. An addition of H_2 to the mixture gases of C_2H_2 and Ar during growth seems to increase the length of CNTs as well as to decrease their diameters. At the Ar:H_2 ratio of 75:75, many CNTs are of ~3 walls. Such long and thin MWCNTs are expected to be very useful for their applications, in particular, to field emitters due to their high aspect ratios.

5. References

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