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Gravity-Assisted Chemical Vapor Deposition of Vertically Aligned Single-Walled Carbon Nanotubes

Effects of Temperature and CH_4/H_2 Ratio

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Temperature and CH_4/H_2 ratio of gas-flow rates are the two factors that strongly affect the qualities of vertically aligned single-walled carbon nanotubes (SWCNTs) in gravity-assisted chemical vapor deposition (CVD). The qualities of SWCNTs and other carbon products grown by gravity-assisted CVD were characterized by scanning electron microscopy and Raman spectroscopy. At temperatures between 850 and 900°C, SWCNTs of very good quality stand alone on the substrate. At other temperatures, nanofibers or irregular islands of carbon are present on the substrate. The CH_4/H_2 ratio influences the quality of SWCNTs more abruptly than temperature. At low ratio, no carbon nanotube is formed. The window of CH_4/H_2 ratio for the growth of vertically aligned SWCNTs ranges from 160:80 to 160:40. At a ratio higher than 160:40, multiwalled CNTs replace SWCNTs and become the dominant product.

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The growth of aligned single-walled carbon nanotubes (SWCNTs) on flat substrates has recently become an attractive method for fabricating nanotube-based devices such as nanotransistors,[1] nanoelectrodes for DNA detection,[2] and electron emitters for display.[3] The alignments of SWCNTs are divided into horizontal (parallel to the substrate) and vertical (perpendicular to the substrate). The horizontal alignment has been achieved either by applying an electric field between two electrodes[4,5] or by controlling the direction of the gas flow.[6,7] The vertical alignment of multiwalled carbon nanotubes (MWCNTs) has been realized in the past few years. In contrast, the growth of vertically aligned SWCNTs on various substrates remains challenging. Until recently, the vertical alignment of SWCNTs has been achieved by applying a dc bias in plasma-enhanced chemical vapor deposition (PECVD)[8,9] or by using the gravity force in CVD.[10] In the dc-biased PECVD method, SWCNTs are aligned in the direction of the electric field, as reported by Maschmann et al.[8] One drawback of this method is a decrease in the amount of SWCNTs due to the bombardment of positively charged hydrogen ions that are accelerated by a negative dc bias. A very simple method for growing vertically aligned SWCNTs on Co/Si(100) based on the gravity effect in the CVD process was recently developed.[10] In the gravity-assisted CVD method, the Co/Si(100) substrate is tilted such that its surface normal points downward, enabling SWCNTs to align in the direction of gravity. The success of growing vertically aligned SWCNTs is attributed to the formation of liquid drops of the metal catalyst at high temperatures. The SWCNTs are precipitated out of the liquid-metal drops and aligned with gravity.[10]

The merit of the gravity-assisted CVD process is its simplicity as a method for constructing three-dimensional electronic devices that require vertical SWCNTs. The characteristics of the gravity-assisted CVD process thus deserve further investigation. In this paper, the effects of growth temperature and CH_4/H_2 ratio on the growth of vertically aligned SWCNTs using the gravity-assisted CVD process are discussed.

Experimental

Vertically aligned SWCNTs were grown on Co/Si(100) by gravity-assisted CVD, shown schematically in Fig. 1. A Co catalyst 1 nm thick was deposited onto p-Si(100) by magnetron sputtering. The as-deposited Co/Si(100) substrate was cleaned by alcohol and deionized water before it was placed in the center of the CVD furnace. An Al_2O_3 holder designed to place samples is ~0.5 cm deep and 3×5 cm^2 in area. The as-cleaned substrate was then placed on an Al_2O_3 holder with its surface pointing downward in the CVD furnace and then heated from room temperature to the growth temperate (800–1000°C) in the CVD furnace with argon flow. The as-heated substrate was maintained at the selected temperature in an atmosphere of H_2 for 10 min before the growth of SWCNTs to remove any metal oxide. An H_2/CH_4 mixed gas was fed into the furnace for 1.5 min to grow SWCNTs hung on the Co/Si(100) substrate. The CH_4/H_2 ratio varies from 160:160 to 160:20 for growing vertically aligned SWCNTs at a fixed growth temperature. The surface morphologies of the as-grown samples were characterized using a JEOL JSM-6500F field-emission scanning electron microscope (FESEM). Raman spectra were obtained to characterize the chemical information of the as-grown products, using a high-resolution micro-Raman system (Renishaw 2000 Raman microscope) with a laser source at a wavelength of 532 nm.

Results and Discussion

Effect of temperature.— The growth of SWCNTs in a CVD process has been shown to be highly sensitive to temperature.[11,12] Temperature is considered to be a major factor in the gravity-assisted CVD process because of a similar chemical reaction in the synthesis of SWCNTs. Figures 2a-e show a series of SEM images regarding the morphologies of as-grown Co/Si(100) at various temperatures. The growth time (1.5 min) and CH_4/H_2 ratio (160:80) were kept constant while the temperature was varied. At 800°C, nanoscale fibers with morphologies that are similar to those of carbon nanotubes form on the Si substrate. The morphologies of SWCNTs appear on the substrate at temperatures higher than 850°C. Vertically aligned SWCNTs of good quality can be achieved at a growth temperature of 900°C. The directions of SWCNTs are within 30° from

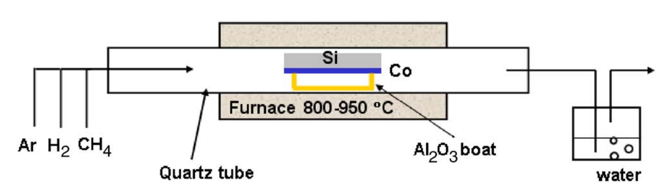

Figure 1. (Color online) Schematic of the furnace design for the gravity-assisted CVD process.

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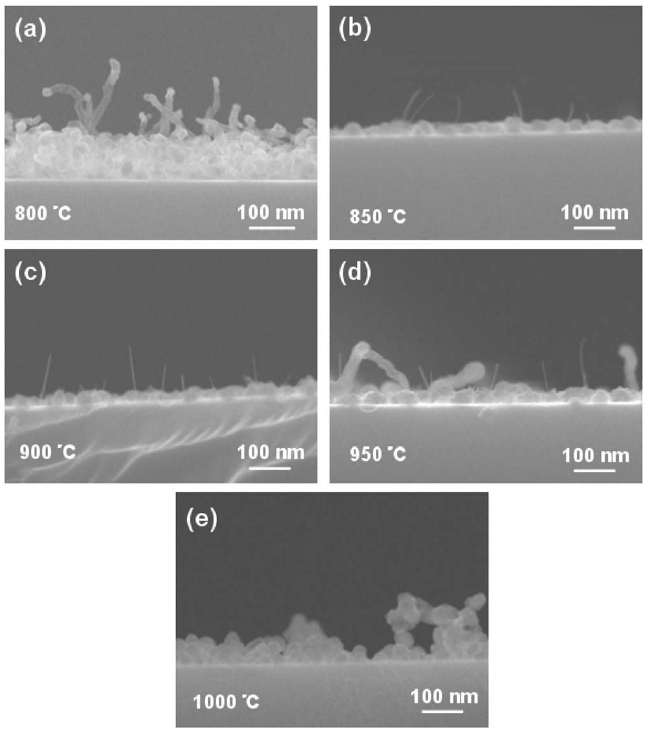

Figure 2. SEM images of CNTs grown on Co/Si(100) at various temperatures: (a) 800, (b) 850, (c) 900, (d) 950, and 1000°C.

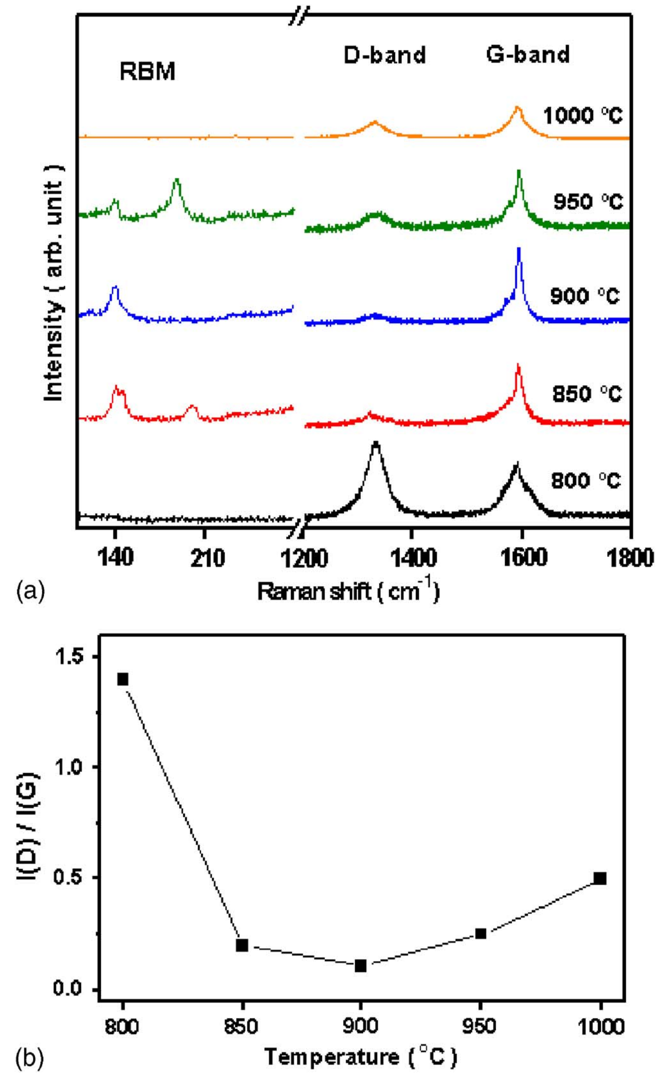

Figure 3. (Color online) (a) Raman spectra of CNTs grown on Co/Si(100) at various temperatures and (b) I(D)/I(G) ratio as a function of growth temperature.

the surface normal. Most SWCNTs orient vertically within 5°, almost aligned with the direction of gravity. The force due to gravity is estimated to be $\sim 10^{-20}$ N.[10] If other forms of larger force were applied, gravity would not lead the direction of SWCNTs. The temperature window for growing vertical SWCNTs are less than 100°C, because some nanofibers with a larger diameter begin to appear at 950°C, as shown in Fig. 2d. At 1000°C, SWCNTs disappear completely. Irregular islands on the substrate, as presented in Fig. 2e, replace the nanofibers in Fig. 2d.

Figure 3a shows a series of Raman spectra that correspond to the nanoscale structures presented in Fig. 2a-e. Two major peaks centered at 1590 and 1320 cm^{-1} appear at 800°C. No radial breathing mode (RBM) signals in the range of 100–300 cm^{-1} were observed, which are the evidence for the existence of SWCNTs.[13] The G-band peak at around 1590 cm^{-1} has been attributed to the tangential modes of a graphite structure in CNTs.[14,15] The D-band peak at around 1320 cm^{-1} arises from the presence of disordered graphite and the defects of CNTs.[14,15] The ratio of D-band to G-band intensity $[I(\mathrm{D})/I(\mathrm{G})]$ is used to characterize the chemical information of CNT-related nanostructures.[16,17] The ratio I(D)/I(G) at 800°C is about 1.4, which corresponds to MWCNTs, according to previously published results for MWCNTs.[18] At 850°C, the Raman spectrum exhibits two main features. One is the appearance of three RBM signals in the range 100–300 cm^{-1}, indicating the existence of SWCNTs. The RBM peaks are located at 140, 145, and 200 cm^{-1}, corresponding to SWCNTs with diameters of ~1.77, 1.71, and 1.24 nm, as estimated using the equation $d\,(\mathrm{nm}) = 248/[\nu(\mathrm{cm}^{-1})]$,[19] where d is the diameter and ν is the RBM frequency. The other feature is the decrease in the I(D)/I(G) ratio, supporting that no MWCNTs appear with SWCNTs on Co/Si(100) at 850°C. As the temperature increases to 900°C, a single RBM peak at 140 cm^{-1} appears, corresponding to SWCNTs with a diameter of ~1.77 nm. At 950°C, two RBM signals are observed at 140 and 186 cm^{-1}, corresponding to SWCNTs with diameters of ~1.77 and 1.33 nm, respectively. The increase in I(D)/I(G) ratio indicates that the chemical constituent of the nanofibers in Fig. 2e is carbon. Notably, the RBM signals are completely absent at 1000°C. Only D and G peaks are present in the Raman spectrum, implying that the irregular islands in Fig. 2e mainly consist of sp^2 carbon bonds. Very probably, carbon nanofibers dominate at 1000°C, linking with each other and forming the irregular islands.

Figure 3b plots the I(D)/I(G) ratio as a function of growth temperature. The I(D)/I(G) ratio declines substantially from 1.4 to 0.2 as the growth temperature increases from 800 to 850°C, because of the appearance of SWCNTs at 850°C. The I(D)/I(G) ratio reaches a minimum value of 0.11 at 900°C before rising back to 0.5 at 1000°C, supporting the fact that the SWCNTs grown at 900°C are of the highest quality. The increase of I(D)/I(G) ratio reveals that the quality of SWCNTs becomes worse at temperatures higher than 900°C, which has been attributed to the thermal pyrolysis of CH_4 to amorphous carbon (disordered graphite) at high temperatures, as reported by Hornyak et al.[11]

Effect of CH_4/H_2 ratio.— The effect of CH_4/H_2 ratio on the growth of SWCNTs by gravity-assisted CVD at 900°C is thus investigated based on the results in the previous section. Figures 4a-d show SEM images of the as-grown samples at various CH_4/H_2 ratios of gas-flow rates. No CNTs (SWCNT and MWCNTs) were observed at a CH_4/H_2 ratio of 160:160. As the CH_4/H_2 ratio in-

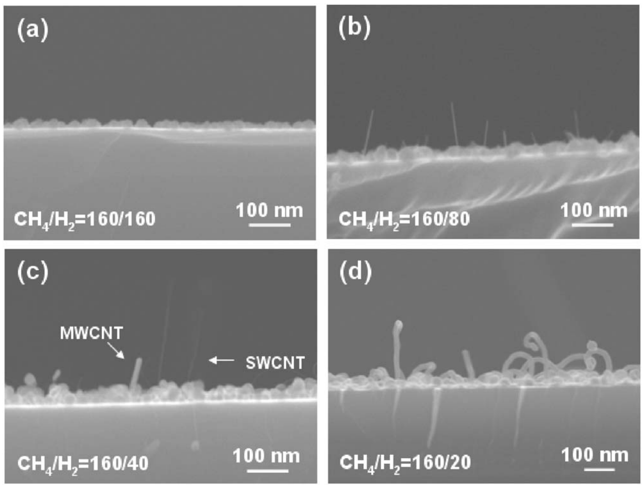

Figure 4. SEM images of CNTs grown on Co/Si(100) at various CH_4/H_2 ratios of gas flow rates: (a) 160:160, (b) 160:80, (c) 160:40, and (d) 160:20.

creases to 160:80, vertically aligned SWCNTs are present, as shown in Fig. 4b. At a CH_4/H_2 ratio of 160:40, SWCNTs and MWCNTs coexist (Fig. 4c). MWCNTs completely replace SWCNTs at a higher CH_4/H_2 ratio of 160:20 (Fig. 4d).

The Raman spectra in Fig. 5 characterize the qualities of CNTs (MWCNTs and SWCNTs). No RBM signals appear at a CH_4/H_2 ratio of 160:160, confirming the SEM observation in Fig. 4a. The weak D-band and G-band signals are attributed to the low carbon supply, which limits the growth of CNTs. At a CH_4/H_2 ratio of 160:80, a strong RBM peak appears at 140 cm^{-1}, corresponding to SWCNTs with a diameter of ~1.77 nm. The low $I(D)/I(G)$ ratio reveals the high quality of SWCNTs. The appropriate carbon concentration leads to the growth of SWCNTs. As the CH_4/H_2 ratio increases to 160:40, two weak RBM peaks appear at 190 and 205 cm^{-1}, corresponding to SWCNTs with diameters of ~1.31 and ~1.21 nm, respectively. The $I(D)/I(G)$ ratio increases to 0.5, suggesting the existence of MWCNTs on the substrate.[20] This result agrees very well with the SEM images in Fig. 4c. At a CH_4/H_2 ratio of 160:20, RBM signals disappear and the $I(D)/I(G)$ ratio is ~0.5, implying the existence of MWCNTs. Increasing the CH_4 concentration causes more carbon to diffuse into the catalysts, reflecting the precipitation of more carbon and consequent MWCNT growth. This finding is consistent with the SEM images in Fig. 4d. The window of CH_4/H_2 ratios for the vertically aligned SWCNTs growth is from 160:80 to 160:40. The growth region of SWCNTs at various CH_4/H_2 ratios is between the growth regions of non-CNT and MWCNT.

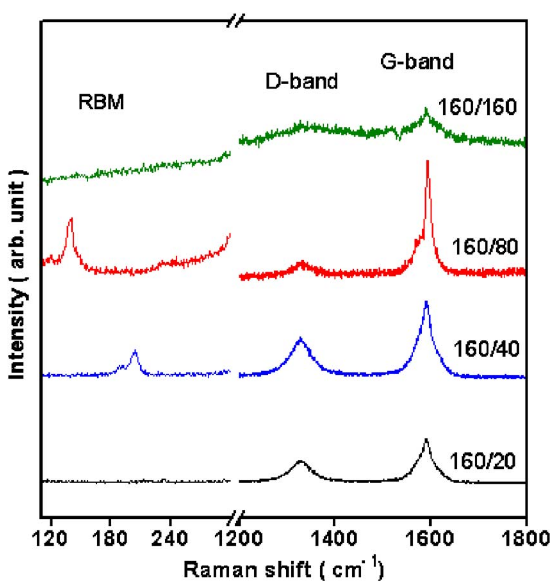

Figure 5. (Color online) Raman spectra of CNTs grown on Co/Si(100) at various CH_4/H_2 ratios of gas-flow rates.

Conclusions

Vertically aligned SWCNTs can be grown on Co/Si(100) at appropriate ranges of temperature and CH_4/H_2 ratios. At temperatures between 850 and 900°C, SWCNTs of very good quality stand alone on the substrate. At other temperatures, nanofibers or irregular islands of carbon are present on the substrate. The window of CH_4/H_2 ratios for the growth of vertically aligned SWCNTs ranges from 160:80 to 160:40. At a low ratio, no CNTs were grown on the substrate. The supply of appropriate amounts of CH_4 and H_2 cause SWCNTs to form. At a ratio higher than 160:40, MWCNTs gradually replace SWCNTs as the dominant species on the substrate.

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