

Growth of Aligned Carbon Nanotubes on Different Metal Substrates

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Abstract. Vertically aligned carbon nanotubes (VACNTs) grown on metal substrates are of great importance for their applications in thermal and electrical devices. However, synthesizing better quality and long CNTs on metal substrates is still a big challenge. We have synthesized vertically aligned multiwalled carbon nanotubes (MWCNTs) on different metal substrates (i.e. copper and iron) by chemical vapor deposition and vertically aligned CNTs with lengths ranging from 2 to 400 μm were obtained. Moreover, the length of CNT on iron substrate has reached over 1mm, which is relatively high CNT arrays using CVD on metal substrate to date.

Introduction

Since the discovery of Iijima in 1991[1], carbon nanotubes (CNTs) have attracted much attention due to the good chemical stability, a high aspect ratio geometry, low coefficient of thermal expansion, high thermal[2] as well as electrical conductivity[3] and mechanical strength[4]. CNTs can be employed as thermal interface materials (TIMs) in microelectronic packaging, electrode materials in energy storage cells[11] and super capacitors, field emission electron sources in flat panel displays[12,13] as well as e-beam lithography equipment and so on[5-10]. As discussed above, high electrical and thermal conductivity at room temperature [14]) are required for these applications, which usually need metal substrates (e.g. copper or iron) to connect with CNTs. However, the majority substrates for CNT growth are still the silicon [23-25], because better quality and high array can be easily got on silicon substrate by water-vapor-assisted CVD. Afterwards, CNT has to be transferred to the metal substrate for any applications requirements. As for the metal substrate, because of a high surface energy, catalyst will easily diffuse into the metal substrate and do not form nanoparticles, which has already been observed on Fe and Cu substrate [15]. Although a few papers have reported syntheses of CNT on various metal substrates, there are still big challenges [16-21] in this issue, such as poor alignment and more defects in the synthesized CNTs[22]. Thus, synthesizing high-quality VACNTs on different metal substrates is urgently needed. In this paper, we report an easy progress on fast synthesis of high-quality VACNTs on different metal substrates through a common thermal CVD process without water-vapor-assisted.

Experimental Section

Materials. Industrial-grade acetylene, industrial-grade argon and hydrogen for the synthesis of our CNTs in which industrial-grade acetylene was carbon source. A thin layer of 2nm Fe was used as catalyst and 30nm Al_2O_3 was used as a buffer layer on the metal substrate. Copper foil with thicknesses of 132 μm , iron foil with thicknesses of 380 μm , copper column with thicknesses of 1.2cm and iron column with thicknesses of 0.9cm were used as metal substrates for aligned CNT growth.

CVD Reactor Operations. We used CVD for synthesis of aligned CNTs, which was performed in a horizontal quartz tube (5 cm in diameter and 100 cm in length) housed in a single-zone furnace as shown in Figure 1.

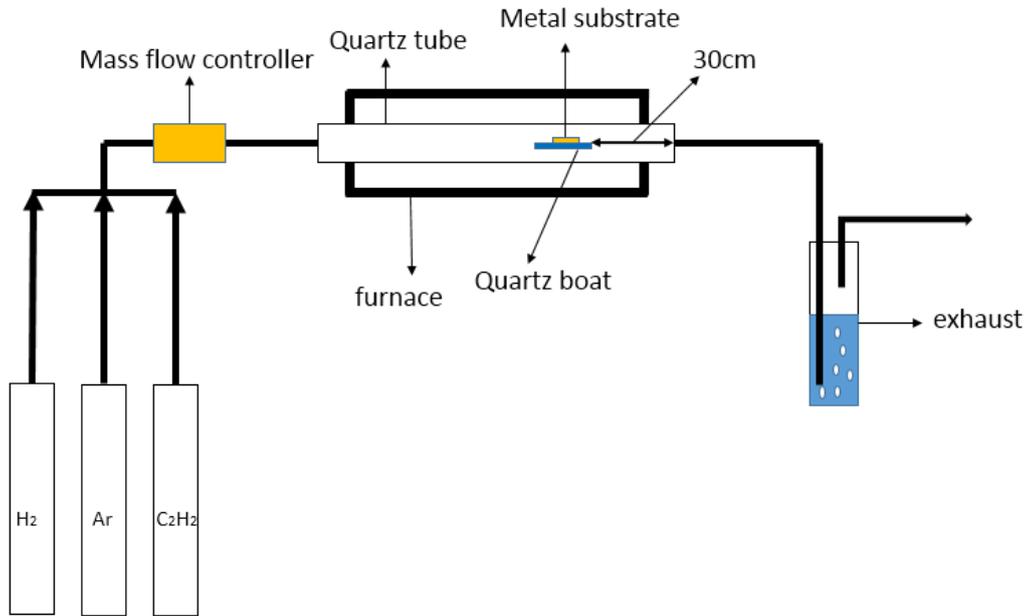


Figure 1. Experimental setup for aligned CNT synthesis by chemical vapor deposition.

The position of quartz boat (4 cm wide and 7 cm long) was placed in the quartz tube 30cm to the tail, where the acetylene can be deposited better. The substrates used in this study were placed in the middle of the boat. Argon flow in the quartz tube about 5min to exhaust air in tube. Then, the CVD reactor was heated and the reaction started in the CVD reactor at room temperature. Hydrogen was inlet into the reactor at different temperatures (500°C, 560°C and 620°C). CVD growth of aligned CNTs was carried out at about 750-850 °C when the source gases were inlet with the flow rates of 24, 142 and 303sccm (standard cubic centimeter per minute) for acetylene, hydrogen, and argon respectively. The flow of the ethylene/hydrogen/argon mixture was maintained for the entire growth period ranging from 10 to 60 minutes on different substrates.

Results and Discussion

Effect of Different Temperature to Supply H₂

Here we have synthesized VACNTs on various substrates. For the effect of H₂ inlet at different temperature, we use copper as the sample to explore the mechanism.

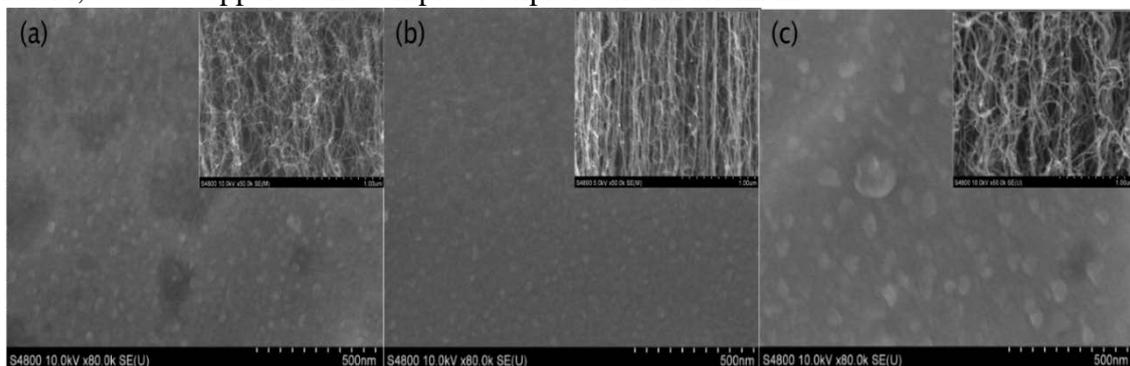


Figure 2. SEM images of the catalyst morphology and aligned CNT layer on copper foil, in which H₂ were inlet at different temperature (a) 500°C (b) 560°C (c) 630°C

Figure 2 shows that the morphology of catalyst and **aligned** CNT layer on copper foil, in which H₂ were inlet at different temperature. From the results, we can see the catalyst particles are more

uniform when inletting H_2 at $500^\circ C$ and much denser aligned CNTs were obtained. Ostwald ripening occurred when H_2 was inlet at $630^\circ C$ due to the surface tension between the particles, which makes small particles incorporate in large particles and leads to messy CNT arrays.

Effect of Growth Time

Also use copper as the sample, Figure 3 shows SEM images of CNTs grown on the copper foil substrate for different growth times. The relationship between the thickness of the aligned CNT film and the growth time at $750^\circ C$ is shown in (g). The growth time was from 5 min to 60 min. The decreased growth rate could be attributed to the catalyst lost of activity.

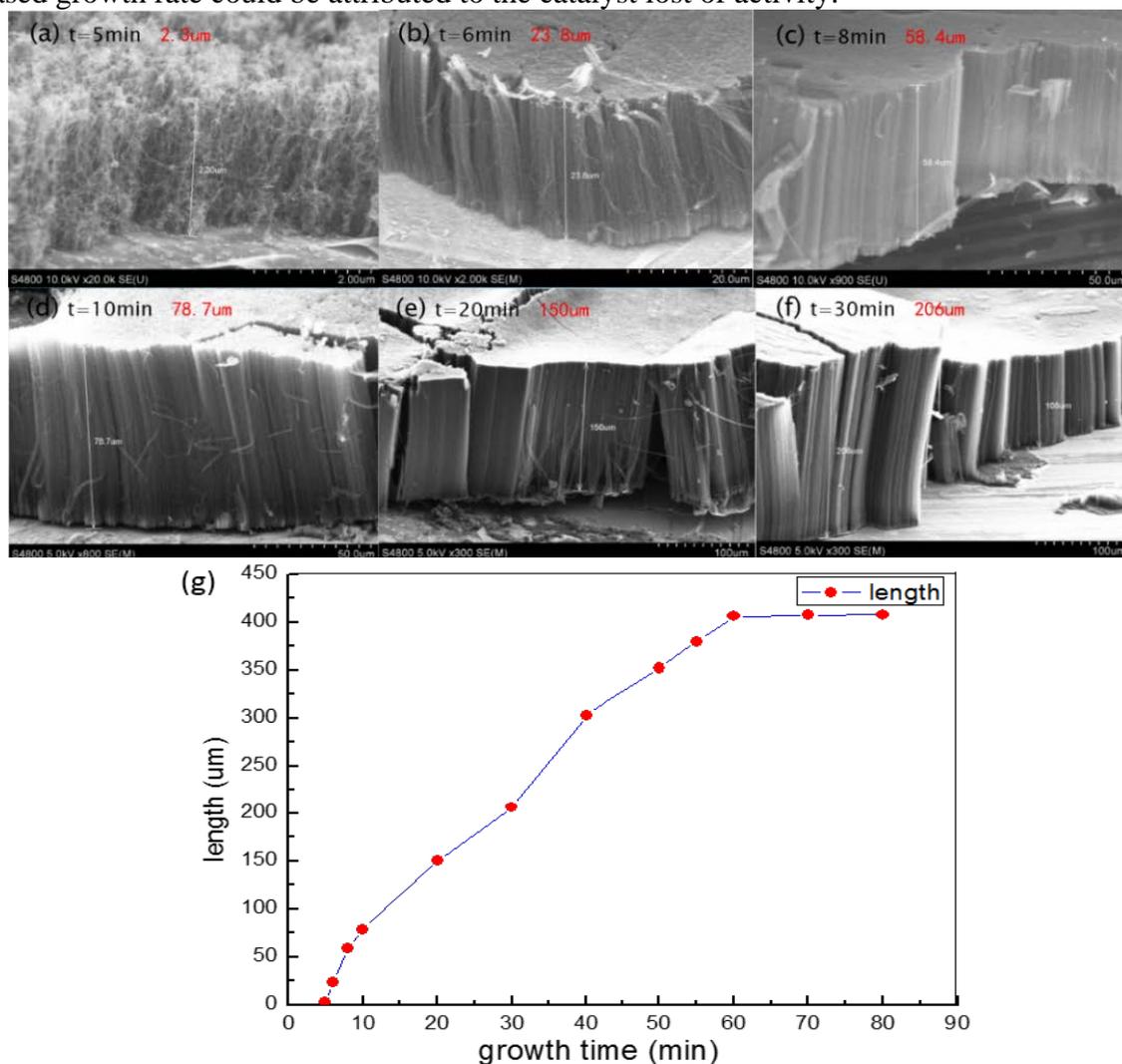


Figure 3. SEM images of aligned CNT layer on copper foil substrate for various growth times: (a) 5min, (b) 6min, (c) 8min, (d) 10 min, (e) 20min and (f) 30min, (g) Effect of growth time on CNT film thickness. (23sccm C_2H_2 , 143sccm H_2 , 303sccm Ar; growth temperature, $750^\circ C$.)

Effect of Growth Temperature

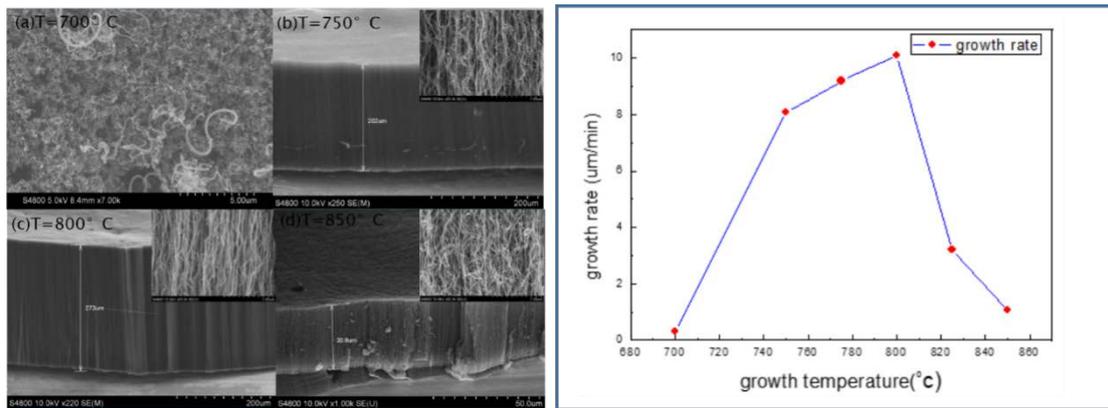


Figure 4. SEM images of aligned CNT layer on copper substrate grown at different temperatures: (a) 700°C, (b) 750°C, (c) 800°C, and (d) 850°C. (g) Effect of growth temperature on growth rate. (23sccm C₂H₂, 143sccm H₂, 303sccm Ar; growth time, 25 min.)

Figure 4 shows SEM images of CNTs grown on copper foil substrate at increasing growth temperatures. At 700°C, the temperature was not sufficiently high for the acetylene to be deposited on the substrate, and no aligned CNTs were found (Figure 4a). At a temperature of 800°C, the aligned CNT film was 272 μm, and the growth rate was 10.09 μm/min, which was faster than other arrays (8.08 μm/min, 750°C; 1.06 μm/min, 850°C). What's more, much longer and denser aligned CNTs were obtained at 800°C. The relationship between the growth rate of the CNT layer and the growth temperature is shown in (g) Figure 5.

Effect of Different Substrate

30nm buffer layer (Al₂O₃) and 2nm catalyst (Fe) catalyst system are deposited on copper foil, iron foil, copper column and iron column, and we have synthesized aligned multiwalled carbon nanotubes (MWCNTs) on all of them. Figure 5 shows different thickness on different metal substrate and the pattern of the arrays. It is clear that the diameter of CNTs on iron substrate were thicker than other substrates. It was also verified by TEM (Figure 6) and the detailed structure of the CNTs also was studied by it. We found that the CNTs were of different sizes but had a similar structure because of same thickness of catalyst and buffer layer. The thickness of CNT on iron column reached 1.03mm, which is relatively high CNT arrays on metal substrate to date.

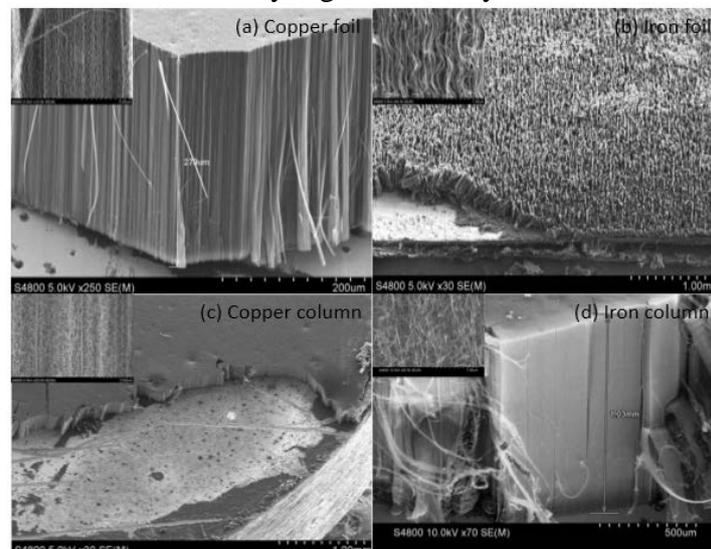


Figure 5. SEM images of aligned CNT layer on different substrate

However, as the mixture of amorphous carbon and CNTs, CNT arrays on iron foil and iron

column have more defects than the array on copper foil and copper column. As in Figure 7, Raman spectra show that CNTs on copper foil were better than other metal substrates.

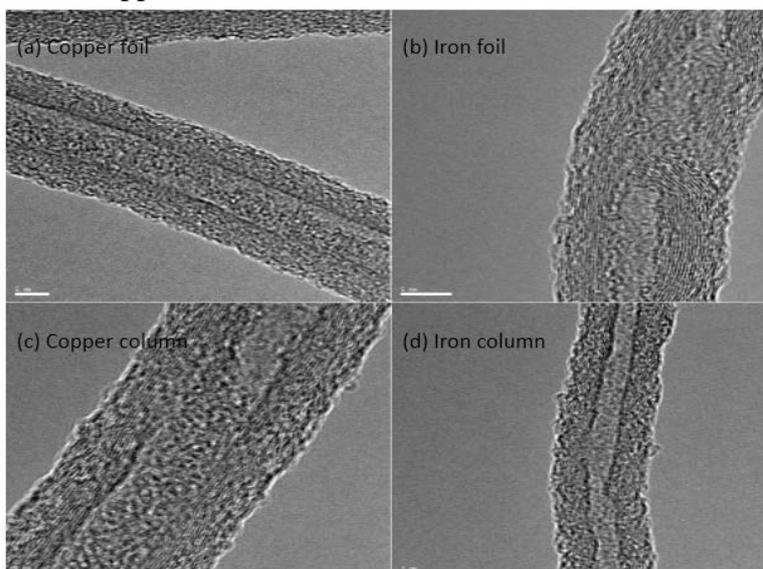


Figure 6. Detailed structure of aligned CNTs by TEM

We can see that the purity of CNT on iron foil was low and defects on column were more than on foil. The intensity ratio between bands D and G (I_D/I_G) is 0.6 and 0.8 for CNTs grown on copper foil and copper column, while for CNTs grown on iron foil and iron column I_D/I_G is higher than 1.0. So we can illustrate the higher degree of defects for CNTs grown on iron substrate.

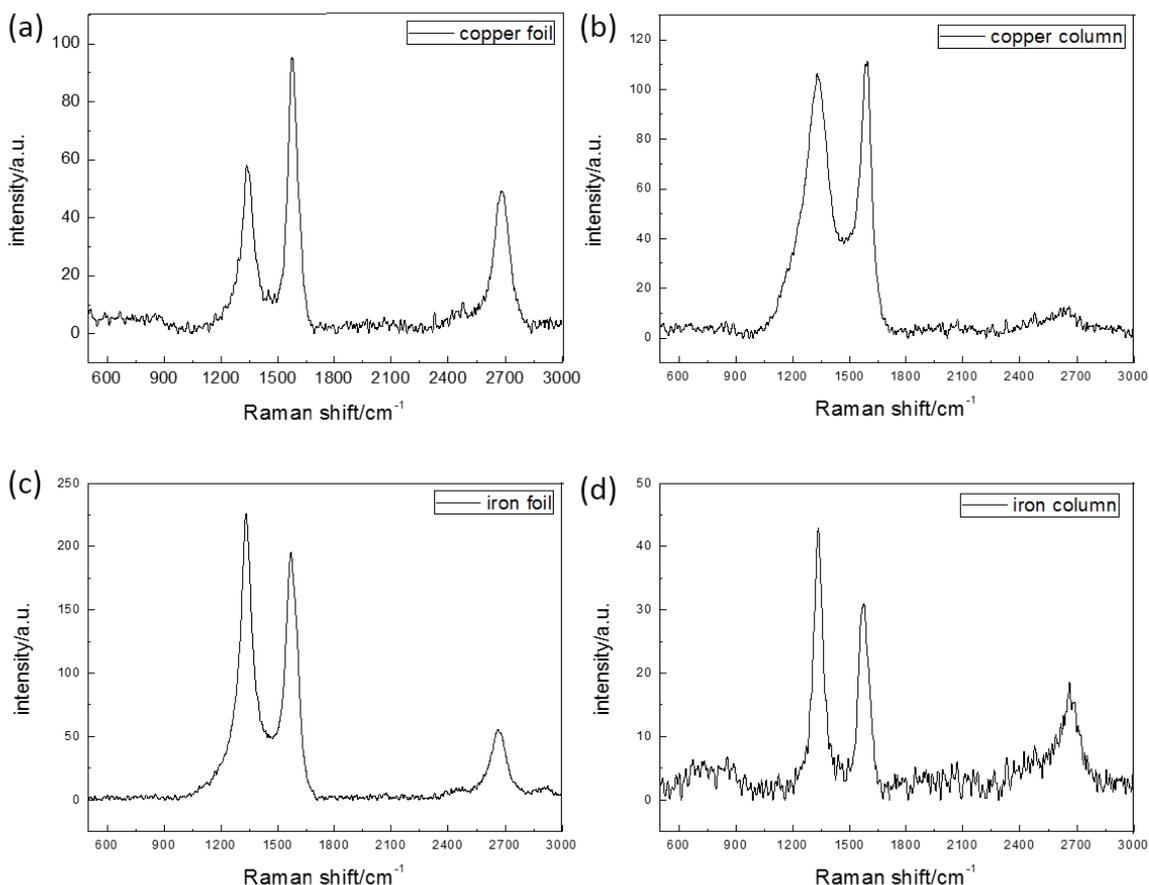


Figure 7. Raman spectra of aligned CNTs

Conclusions

Because of the high surface energy, it was a big challenge to synthesize better CNTs on metal substrates. Fortunately, we have achieved this goal and successfully grew aligned MWCNTs on different metal substrate by depositing optimal 30nm buffer layer (Al_2O_3) and 2nm catalyst (Fe) catalyst in this system. Ostwald ripening easily occurred that H_2 inlet at 630°C . SEM and TEM showed that the diameter of CNTs on iron foil and iron column wider than on copper. With this proportionate gas (23sccm C_2H_2 , 143sccm H_2 , 303sccm Ar) and proper growth temperature (800°C), longer and better arrays were obtained (>1mm) on metal substrate that were relatively high to date. This work can be extended in other different metal substrates. Our efforts in these directions are now underway.

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