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Aligned millimeter-long carbon nanotube arrays grown on single crystal magnesia

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Abstract

Single crystal magnesium oxide (MgO) was found to be very beneficial to the growth of aligned carbon nanotube (CNT) arrays as long as 2.2 mm by chemical vapor deposition. Before growth, a thin film of catalyst (iron) was coated on the MgO by magnetron sputtering. Scanning electron microscopy was used to study the alignment and length, and transmission electron microscopy was used to exam the wall numbers, diameter, and graphitization. It was found that the number of walls as few as two can be controlled by the catalyst film thickness, whereas the length is a combined result of gas pressure, temperature, and time during growth. Water was found not to be a factor to the length of CNTs grown on MgO, but a significant factor when sapphire was used as the substrates.

Keywords: Carbon nanotubes; Sputtering; Annealing; Chemical vapor deposition

1. Introduction

Since the discovery of carbon nanotubes (CNTs) by Iijima in 1991 [1], researchers have been very actively trying to gain controls on length, diameter, alignment, location, periodicity, number of walls, chirality, etc. [2–13]. Even though a tremendous progress has been achieved in some of the aspects during the past years, it is not until recently that Iijima et al. succeeded on growing very long (about 2.5 mm) aligned single-walled carbon nanotubes (SWCNTs) on alumina-coated single crystal silicon substrates by water-assisted chemical vapor deposition (CVD) [14], in which water was believed to be crucial to keep the catalyst active leading to the long length. The long length, also meaning very high purity, is very much desired for not only applications for high strength but also basic studies such as the effect of impurity on magnetic properties. Unfortunately, we were not able to reproduce Iijima's results, but discovered that aligned CNTs as long as 2.2 mm with a pre-determined number of walls including double wall can be grown on single crystal magnesium oxide (MgO) by CVD using ethylene (C_2H_4) as the feeding gas and hydrogen (H_2) as the dilution gas. In this study, water was also used in independent experiments and did not show any effect on the length of the CNTs on MgO, but did show a significant effect on the growth of CNTs on sapphire.

2. Experimental

The experiments described in this work are comprised of three main steps: (i) preparation of catalyst film of iron (Fe) on single crystal MgO by magnetron sputtering, (ii) annealing of catalyst film to form nanoparticles, and (iii) growth of aligned CNTs by CVD.

2.1. Catalyst film preparation

Single crystal MgO with orientations of (100), (110), and (111) were cut into $5 \times 5 \times 0.5\ mm^3$ and cleaned in

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alcohol by ultra-sonication first, then loaded into the sputtering chamber for catalyst film deposition. A base pressure of 3×10^{-6} Torr was obtained before Argon gas was introduced for sputtering Fe film at about 3 mTorr. The sputtering was normally for a few seconds to about 20 min to achieve catalyst film thickness of 0.2–50 nm depending on time.

2.2. Annealing of catalyst film to form Fe nanoparticles on MgO

The annealing and growth steps were carried out in a horizontal tube furnace with a quartz tube of one inch inner diameter. The catalyst-coated MgO was loaded into a small quartz boat and pushed to the center of the furnace, then the furnace was pumped down to about 1 mTorr by a rotary pump, followed by heating to 745 °C within 10 min, then supplying flowing H_2 gas (100 sccm) to reach a pressure of 200 Torr and kept at the temperature and pressure for 10 min, which is the optimal combination resulted from many experimental runs.

2.3. Growth of CNTs by CVD

Immediately after annealing, the furnace was pumped down to about 1 mTorr, followed by introducing flowing gases of H_2 (100 sccm) and C_2H_4 (110 sccm) with the pump turned off. When the pressure reached at one atmosphere (about 760 Torr), a valve was open to atmosphere to maintain the pressure inside the furnace at 760 Torr. The growth was carried out at different temperatures (715–760 °C) and length of time (5–60 min) even though the annealing was always at 745 °C for 10 min as described above.

After growth, scanning electron microscope (SEM, JEOL JSM-6340F) was used to characterize the length and alignment of the CNTs. Transmission electron microscope (TEM, JEOL 2010F) was used to characterize the wall numbers, diameter, and graphitization.

3. Results and discussion

It was found that the pressure during annealing step is a very important factor for the subsequent growth of long CNTs. When the annealing was done below 120 or above 500 Torr, CNTs did barely grow, which is probably due to a strong effect of the pressure on the break up of Fe film into particles. In the range of 120–500 Torr, CNTs grew into different length. The longest CNTs of about 2.2 mm, as shown in Fig. 1(a), were achieved with an optimal annealing pressure at 200 Torr with the optimal growth parameters of 100 sccm H_2, 110 sccm C_2H_4, 745 °C, 760 Torr, and 45 min described in detail in the next paragraph. The SEM images shown in Fig. 1(b)–(d) were taken with a 30° tilting angle. From the low magnification SEM

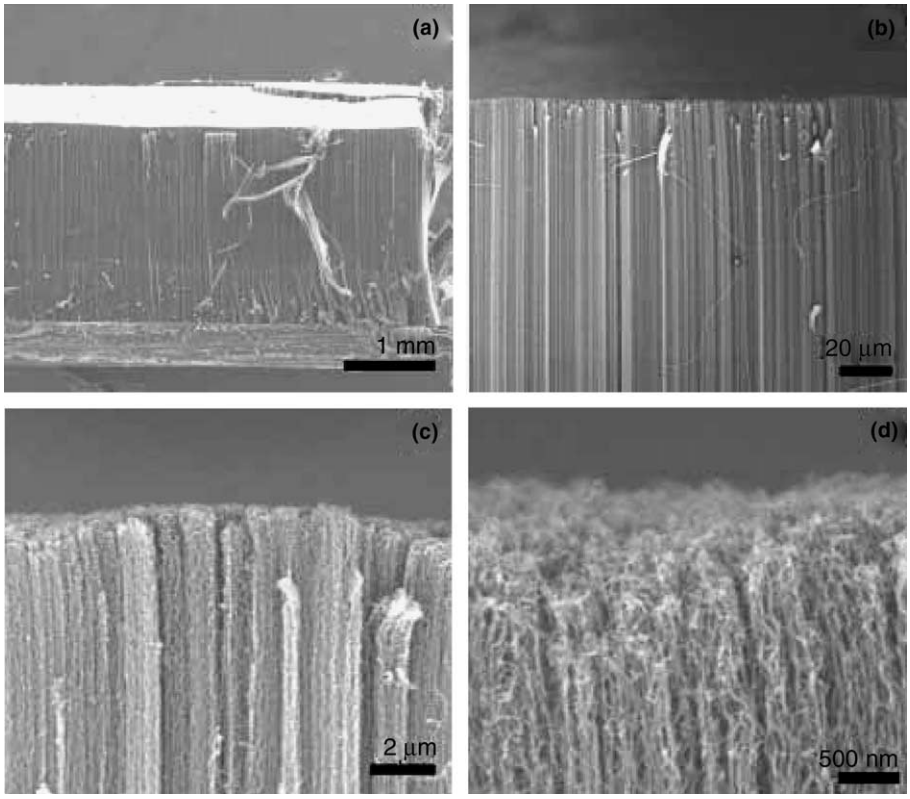

Fig. 1. SEM images of CNTs grown on single crystal MgO substrates coated with Fe film. (a) Low magnification showing the length of CNTs and the thickness of MgO substrate (500 μm); (b) medium magnification showing the good alignment; (c) and (d) high magnification showing the wavy nature of the alignment.

image as shown in Fig. 1(a) and (b), it is clear that the alignment is good and the length is long. From the high magnification SEM image shown in Fig. 1(c) and (d), it is seen that the tubes have very small diameter, are curved, and intertwined with each other in the nanoscale.

The CNT growth was very sensitive to the growth conditions including flow rate of feeding gases, gas pressure and temperature at the growth zone during growth, and growth time [15]. It was found that a combination of 100 sccm H_2 with 110 sccm C_2H_4 is the optimal gas supply, any unilateral adjustment larger than 20% resulted in no CNTs growth at all. Fig. 2(a) shows the CNTs length dependence of the gas pressure with the other growth conditions fixed at 100 sccm H_2, 110 sccm C_2H_4, 745 °C, and 25 min. The length is obviously related to the carbon supplies since higher pressure provides more carbon atoms. For setting up simplicity, we did not run experiments into pressure higher than 760 Torr. Fig. 2(b) shows the CNT length dependence of growth temperature when the other growth conditions fixed at 100 sccm H_2, 110 sccm C_2H_4, 760 Torr, and 25 min. When the temperature is too low, there is not enough carbon supply from the incomplete decomposition of C_2H_4, whereas too high temperature does not provide enough carbon supply either since C_2H_4 decomposes at the place too far away from the substrates. Fig. 2(c) shows the CNTs length dependence of the growth time with the other growth conditions fixed at 100 sccm H_2, 110 sccm C_2H_4, 745 °C, and 760 Torr. It is difficult to understand why longer time resulted in short length. We speculate that there is some oxygen in the system so that the catalyst can only last for 45 min. At the beginning, the growth is much faster than the oxidation so we get quick growth. With growth going on, the catalyst is being consumed. After the catalyst is completely consumed at 45 min, the growth stops, only oxidation continues. The CNTs become shorter with time longer than 45 min. The source of oxygen may be due to a very minor leakage in the system or minor impurity in the gases. Further study in this aspect is in progress. So the best combination for the longest CNTs of 2.2 mm is: 100 sccm H_2, 110 sccm C_2H_4, 745 °C, 760 Torr, and 45 min. The multiple data points in Fig. 2 indicate the number of experiments at the same conditions, which shows a very good reproducibility. Independently, water was used and found not to be a factor to the length when MgO single crystal is used, but a significant factor on extending the lifetime of Fe when sapphire is used as the substrate.

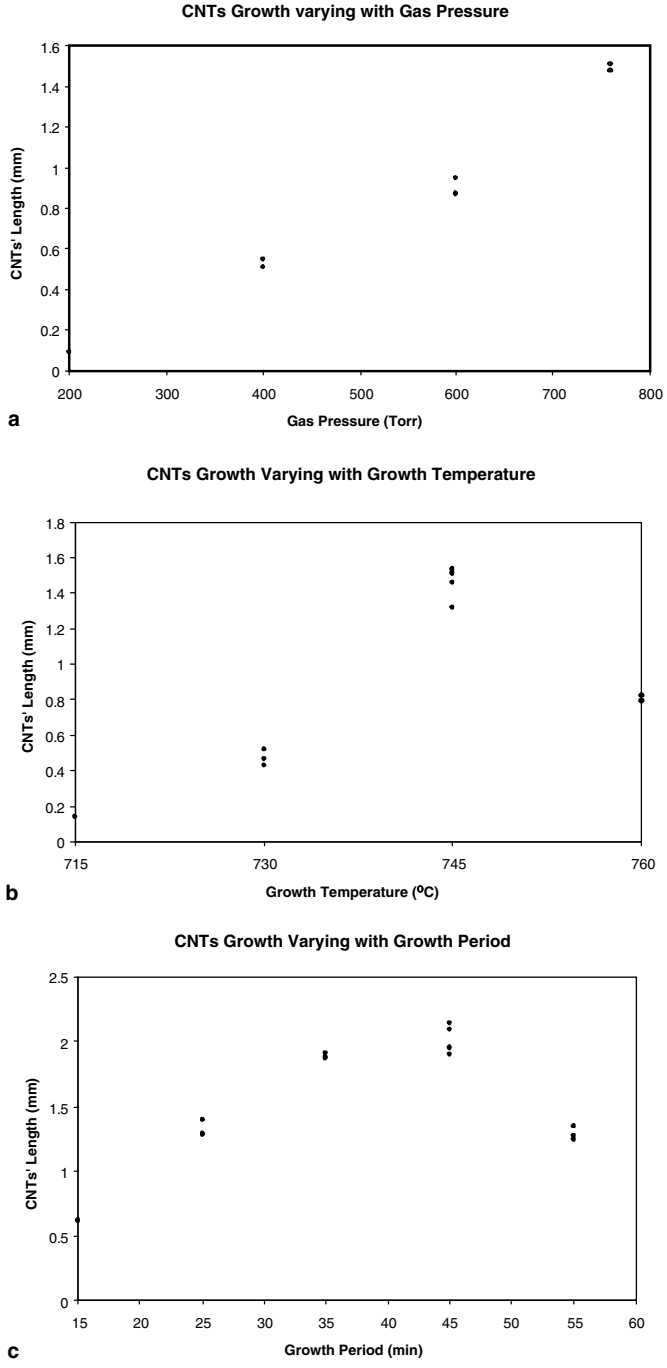

Fig. 2. CNTs length dependence of (a) the gas pressure; (b) the growth temperature; and (c) the growth time.

It is a well-known fact that the catalyst size determines the diameter of the final CNTs. To demonstrate whether we can achieve long length of any diameter, we deposited catalyst film with 0.4, 0.8, and 1.2 nm thickness on MgO. After growth, we studied the microstructures of the CNTs using high resolution TEM. As usual that the thickness of catalyst films affect the outer diameter, but surprisingly the catalyst thickness also controlled the number of walls. In Fig. 3(a), it is shown that the CNTs are free of catalyst particles, consistent with the previous report [14]. For a 0.4 nm catalyst film, the majority of CNTs are double wall (DWCNTs) as shown in Fig. 3(b). For a 0.8 nm catalyst film, the CNTs are mostly three-wall as shown in Fig. 3(c) with a small quantity of four-wall. For a 1.2 nm catalyst film, the majority of the CNTs are four- and five-wall as shown in Fig. 3(d). We also tried to grow single wall CNTs by depositing catalyst film thinner than 0.2 nm, but failed. It is worthy pointing out that the thickness accuracy needs to be confirmed. Nevertheless, the trend is valid.

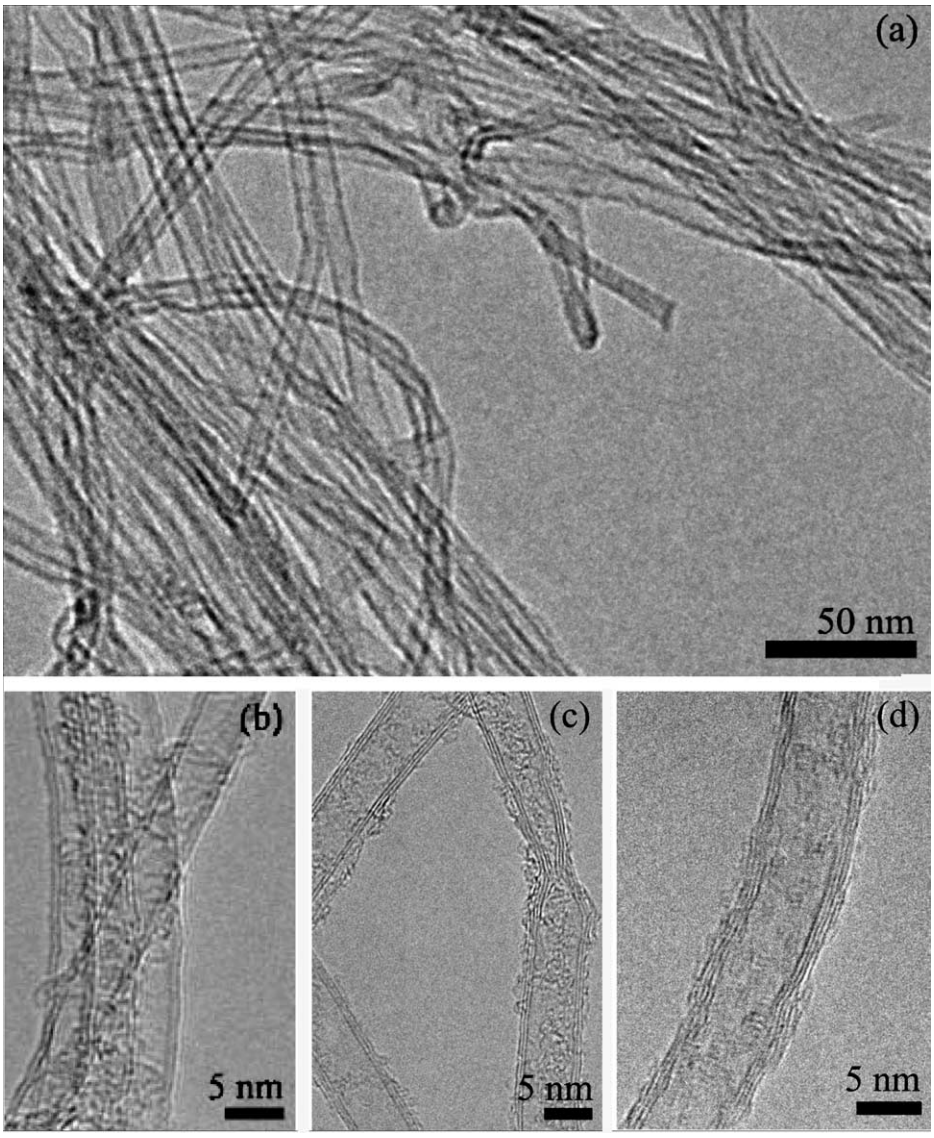

Fig. 3. TEM images of the CNTs grown on MgO substrates in low (a) and high magnification (b–d). (a) Low magnification showing free of catalyst particles; (b) high magnification showing the double wall nature grown from a 0.4 nm Fe film; (c) high magnification showing the three-wall of the CNTs grown from a 0.8 nm Fe film; (d) high magnification showing the four-wall grown from a 1.2 nm Fe film.

Besides the effect of catalyst film thickness on wall numbers and inner and outer diameters, the length of CNTs was also closely related to the thickness of catalyst film. The longest CNTs grown from 0.4 nm film is 80 μm, while the longest from 0.8 nm film is 1.1 mm, and the longest from 1.2 nm film is 2.2 mm. With much thicker catalyst film, the length started to decrease again. When a film of 50 nm was used, we barely got any growth of aligned CNTs. It is probably due to the fact that the film cannot break into isolated particles so the nucleation of CNTs fails.

The orientation of MgO substrates also had an effect on the length. (1 1 0) is the best plane for long length. (1 0 0) plane resulted in a 20% shorter in length, whereas (1 1 1) plane yielded a 55% shorter in length. One of the possible reasons might be the different interaction energies of Fe with the different MgO surfaces leading to different nucleation time of CNTs on different surface planes.

Besides MgO, we also tried other single crystal substrates including sapphire, strontium titanate ($SrTiO_3$), lanthanum aluminate ($LaAlO_3$), yttrium-stablized zirconia (YSZ). Only sapphire worked. The same reason as mentioned above might play a role on the growth of CNTs, plus lattice matching may also play an important role for different substrates.

In this study, Fe was the only catalyst studied. It is reasonable to speculate that if Co or Ni or the alloy of Fe, Co, and Ni or Fe and Mo will be possible to yield much longer aligned CNTs and even SWCNTs.

Since the CNTs have very high purity due to the long length, they may be very useful for the intrinsic magnetic

property and its anisotropy studies and for spinning into high strength carbon nanotube fibers.

4. Conclusion

In summary, we have discovered that single crystal MgO substrate is very beneficial to the growth of aligned CNTs by CVD. Different surfaces of the MgO substrates resulted in different length of CNTs with (110) as the best for obtaining CNTs as long as 2.2 mm. Annealing of the catalytic Fe film between 120 and 500 Torr is very crucial to the nucleation and growth of the final CNTs with 200 mTorr as the optimal pressure. The catalyst (Fe) film thickness determines not only the diameter but also very surprisingly the wall number and the length of the final CNTs. The optimal growth parameters were found to be of 100 sccm H_2, 110 sccm C_2H_4, 745 °C, 760 Torr, and 45 min resulted from many experimental runs. The purity of the CNTs is very high due to the extremely long length.

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