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Low temperature growth of vertically aligned carbon nanotubes by thermal chemical vapor deposition

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Abstract

Vertically well-aligned carbon nanotubes (CNTs) are grown on Fe-deposited silicon oxide substrate at 550°C by thermal chemical vapor deposition of C_2H_2 gas. We employed two-stage heating technique that the reactants heated at 850°C in the first zone flow into the second zone maintained at 550°C for CNT growth. The CNTs have bamboo structure, closed tip, and defective graphite sheets.

1. Introduction

Synthesis of carbon nanotubes (CNTs) has been extensively investigated by a number of research groups, since the first discovery in 1991 [1]. Various methods such as arc-discharge [2,3], laser vaporization [4], pyrolysis [5], and plasma-enhanced [6] or thermal chemical vapor deposition (CVD) [7,8] have been developed. The CVD method has the advantage that CNTs can be grown with high purity, high yield, and good vertical alignment.

One of the most promising applications of CNTs is a field electron emitter in the flat panel displays [9,10]. Sodalime glass deforms at the temperature above ~550°C, thus is commonly used as a low-cost substrate for flat panels. Therefore, the growth of CNTs directly on sodalime glass substrate is a practically very important subject. However, the CNT growth using CVD method usually requires the temperature at least 650°C [7,8].

In this Letter, we report a low-temperature thermal CVD growth of vertically aligned CNTs on iron (Fe) catalytic particles deposited silicon oxide substrate at 550°C using acetylene (C_2H_2) gas. Such a low-temperature growth was made possible by employing the two-stage heating technique that the reactants are heated at 850°C in the first zone and then brought into the second zone maintained at 550°C for CNT growth. This successful CNT growth at 550°C using two-stage heating technique would provide a step forward for applications of CNTs to the field emission displays.

2. Experimental

The 20 mm × 30 mm size p-type Si (1 0 0) substrates with a resistivity of 15 Ω cm were thermally

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oxidized. The thickness of SiO_2 layer was about 300 nm. A 100 nm – thick Fe film was thermally deposited on SiO_2 substrates under a vacuum of 10^{-6} Torr. The quartz CVD reactor consists of two different temperature zones heated separately by resistant heating coils. Fig. 1 is a schematic diagram showing the two different temperature zones of CVD reactor. The first heating (high temperature) zone was maintained at 850°C to activate the reactant gas. The temperature of second heating (low temperature) zone was controlled to be 550°C. The Fe-deposited SiO_2 substrates were loaded with face down direction on a quartz boat placed at the second heating zone. Argon (Ar) was flowed into the reactor in order to prevent the oxidation of Fe while increasing the temperature from room temperature to the reaction temperature. Then the Fe-deposited SiO_2 substrates were pretreated using NH_3 gas with a flow rate of 350 sccm for 30 min before growing the CNTs. The NH_3 pretreatment is a crucial step to control the CNT growth [11]. The CNTs were subsequently grown using C_2H_2 gas with a flow rate of 120 sccm for 20 min. After growth, the reactor was cooled down to room temperature under Ar ambient. The alignment and configuration of CNTs were examined by a scanning electron microscope (SEM) (Hitachi S600). A transmission electron microscope (TEM) (Philips CM20T, 200 kV) was used to determine the structure of CNTs. The CNTs separated from the substrate in acetone using ultrasonic treatment were dispersed on a carbon TEM microgrid. A Raman spectrometer (Renishaw micro-Raman 2000) was also used to identify the structure and the crystallinity of graphite sheets.

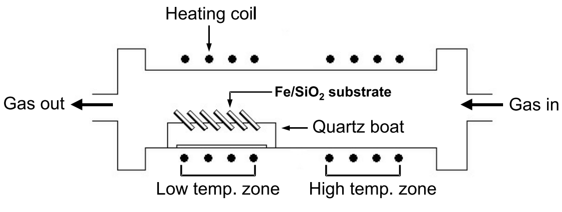

Fig. 1. Schematic diagram of the CVD reactor with two different temperature zones. The Fe-deposited SiO_2 substrates were loaded with face down direction on a quartz boat at the low temperature zone.

3. Results and discussion

Fig. 2a shows the SEM micrograph of the sample. The CNTs are vertically well aligned to the substrate with high density. The length of CNTs is about 1 μm. Fig. 2b is a magnified top view of Fig. 2a, showing the diameter of 20–30 nm and vertically oriented tips. The density of CNTs grown at 550°C is lower than that of vertically aligned CNTs grown on Fe-deposited SiO_2 substrate at 850–950°C [12].

We found few CNTs grown when the temperature of first heating zone was below 850°C. Fig. 3a and b show the surface morphology of Fe particles on SiO_2 substrate after the pretreatment of NH_3 gas, under the condition that the temperature of first heating zone is 700°C and 850°C, respectively. As the temperature increases to 850°C, the size of particles decreases and their density increases. The small-sized Fe catalytic particles could contribute to the CNT growth. Heating at the higher temperature can supply more activated NH_3 gas and/or etching radicals into the second heating zone. When the temperature of second heating zone is below 500°C, there is negligible formation of CNTs. We tried to grow CNTs using one-stage heating method that the growth temperature was

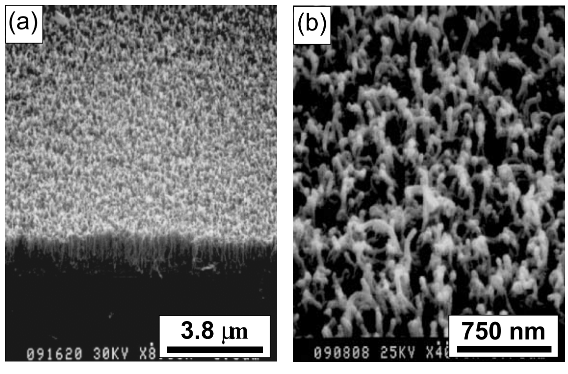

Fig. 2. SEM micrographs of the CNTs grown on Fe-deposited SiO_2 substrate at 550°C. (a) Vertically aligned CNTs with a length of about 1 μm. (b) An enlarged top view of (a), showing the vertically aligned tips.

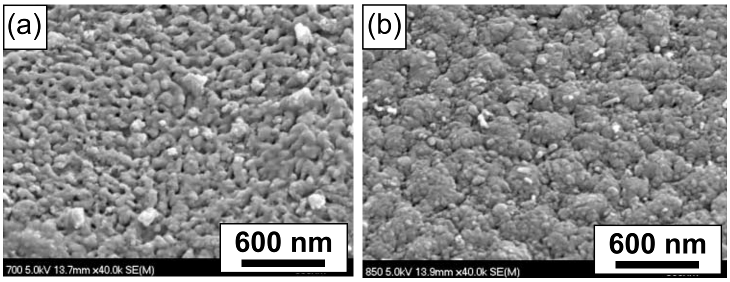

Fig. 3. SEM micrographs for the surface morphology of Fe catalytic particles deposited on SiO_2 substrate after NH_3 pretreatment. The temperature of first heating zone is: (a) 700°C and (b) 850°C.

maintained at 550°C after the pretreatment of NH_3 at 850°C without success. The C_2H_2 molecules are presumably activated or decomposed at 850°C, bringing more reactive hydrocarbons onto the catalytic particles in the growth zone than those heated at 550°C. The results indicate that the activation (or decomposition) in gas phase is an important step in overall reaction, even though detailed mechanism is not known yet. We emphasize that two-stage heating method allows the growth of vertically well-aligned CNTs on SiO_2 substrate at a low temperature such as 550°C, by producing more activated reactants in gas phase compared to one-stage heating method.

Fig. 4a is a TEM image of CNTs grown on Fe-deposited SiO_2 substrate at 550°C, revealing that the diameters are uniformly distributed in the range 20–30 nm. Most of the tips are not encapsulated with catalytic particles (see arrows 1), but some of the tips are encapsulated (see arrows 2). Open roots are indicated by arrows 3. Fig. 4b and c are the high-resolution TEM images, revealing that the bamboo-shaped CNTs are consisted of defective graphite sheets. Fig. 4b shows a tip without any encapsulated catalytic particle (see arrow 9) and the curvature of compartment layer being directed to the closed tip (see arrow 2). Fig. 4c shows another tip with the encapsulated catalytic particle (see arrow 1). The curvature of compartment layer is also directed to the closed tip (see arrows 2).

All of CNTs grown at 950°C have the bamboo structure with a compartment curvature directed to the tip and no encapsulated catalytic particle at the tip [8,12]. But the CNTs grown at 550°C sometimes encapsulate the catalytic particles at the tip, which is in contrast with the CNTs grown at 950°C. Encapsulation of catalytic particles indicates an occurrence of melting of catalytic particles. It was suggested that the existence of the metal in quasi-liquid state at the temperature below the melting point of bulk phase could be attributed to the size effect of metal at nanometer level [13] and/or the interfacial effect between metal and carbon [14]. As the size of catalytic particles decreases, more decrease of melting point is expected. We noticed that the diameter of CNTs grown at 950°C is larger than 60 nm [8,12], while that grown at 550°C is smaller than 30 nm. Therefore, the melted catalytic particles can be possibly encapsulated in narrow inside of CNTs grown at 550°C. The defective graphite sheets of CNTs grown at 550°C are resulted from the low growth temperature.

Fig. 5 shows respective first-order Raman spectrum of vertically aligned CNTs grown on Fe-deposited SiO_2 substrate at 950°C and 550°C. The excitation laser is a 632.8 nm He–Ne laser. The spectrum is consisted of mainly two bands at $\sim$1335 and $\sim$1590 cm^{-1}, respectively. The tangential C–C stretching (G) mode located at 1585 cm^{-1} [15] and a D$'$ band at $\sim$1600 cm^{-1} are observed for the CNTs grown at 950°C, but they appear as one peak at 1595 cm^{-1} for the CNTs grown at 550°C. The D and D$'$ modes indicate the existence of defects or carbonaceous particles on the surface of tubes [16]. The relative peak intensity of D band to G band is about same, but their relative area enhances significantly as the growth temperature decreases from 950°C to 550°C.

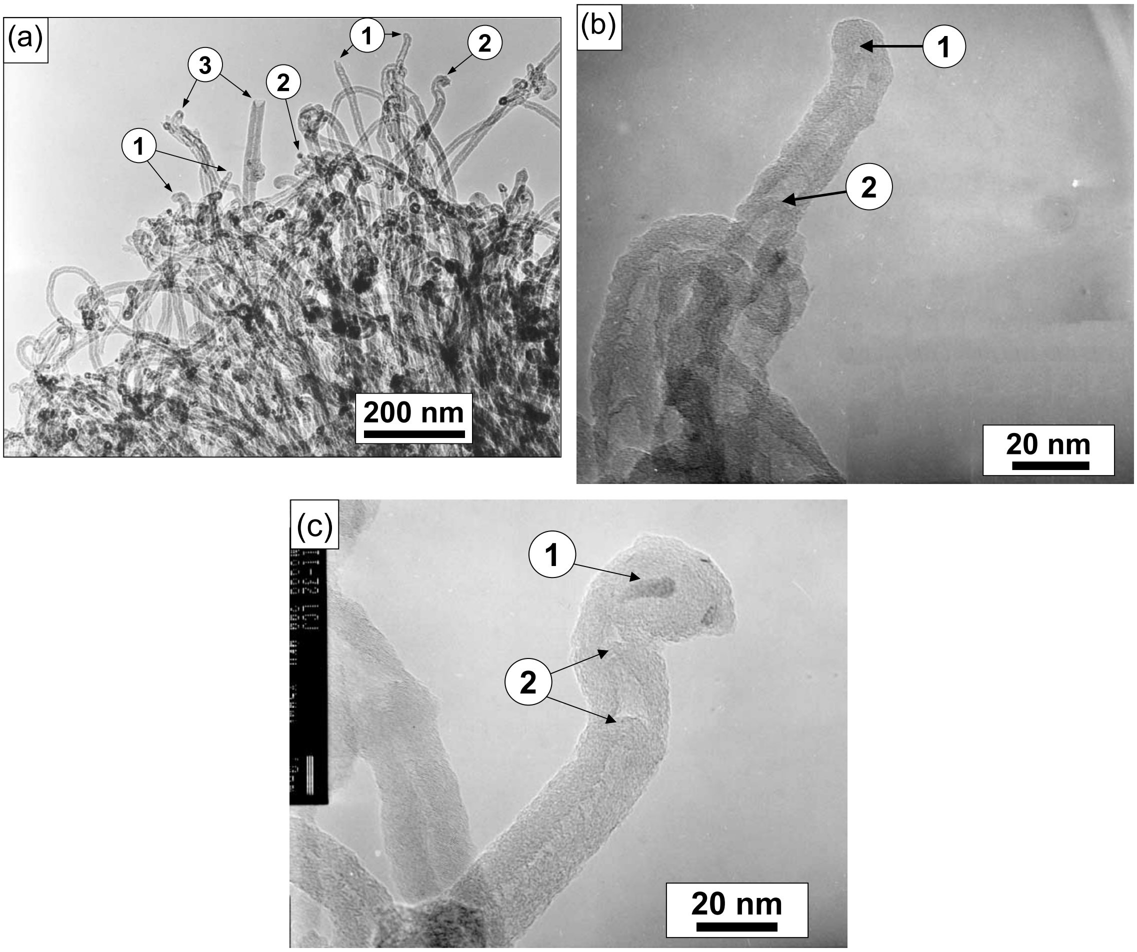

Fig. 4. TEM images of the CNTs grown on Fe-deposited SiO_2 substrate at 550°C. (a) The diameters are quite uniformly distributed in the range 20–30 nm. Most of the tips are not encapsulated with catalytic metal particles (see arrows 1) except a few tips (see arrows 2). Open roots are indicated by arrows 3. (b) A closed tip without any encapsulated catalytic particle (see arrow 1) and the compartment layer with a curvature directed to the tip (see arrow 2). (c) Another tip with an encapsulated catalytic particle (see arrow 1) and the compartment curvature directed to the tip (see arrows 2).

Raman spectrum analysis confirms that the CNTs grown at 550°C have more defects in the graphite sheets than those grown at 950°C.

4. Conclusion

We have grown the vertically well-aligned CNTs at a low temperature such as 550°C, by employing the two-stage heating technique that the reactants are heated in the first zone at 850°C and then brought into the second zone maintained at 550°C for the growth of CNTs. The CNTs have the bamboo structure in which the curvature of compartment is directed to the tip. Most of the CNTs have no encapsulated catalytic particles, but some of them encapsulate the catalytic particles at the closed tip. High-resolution TEM images show that the CNTs are composed of defective graphite sheets. Raman spectrum analysis confirms that the graphite sheets contain more defects than those of CNTs grown at 950°C.

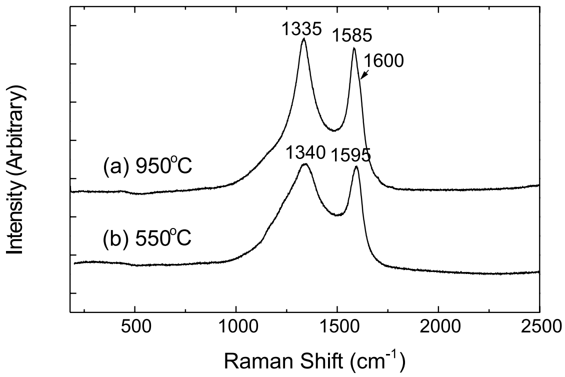

Fig. 5. Raman spectrum for the CNTs grown on Fe-deposited SiO_2 substrate at: (a) 950°C and (b) 550°C.

Acknowledgements

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