Low-temperature growth of carbon nanotubes by thermal chemical vapor deposition using Pd, Cr, and Pt as co-catalyst

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Abstract

Palladium (Pd), chromium (Cr), and platinum (Pt) are used as co-catalysts to decrease the growth temperature of carbon nanotubes to 500–550°C. Pd is found to be the most efficient co-catalyst for the growth of carbon nanotubes on cobalt-nickel catalytic particles deposited on a silicon oxide substrate by thermal chemical vapor deposition using C H . High-resolution transmission electron microscopy reveals the bamboo-shaped carbon nanotubes grown at 500°C using Pd, while the curled carbon nanofibers are grown at 550°C using Cr. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Since carbon nanotubes (CNTs) were first observed [1], there has been extensive research on their synthesis using arc discharge [2], laser vaporization [3], pyrolysis [4], and plasma-enhanced [5] or thermal chemical vapor deposition (CVD) [6,7] methods. Among these synthetic methods, CVD has many advantages such that CNTs can be synthesized with high purity, high yield, selective growth, and vertical alignment. One of the most attractive applications of CNTs is as an electron emitter for flat panel displays. Soda-lime glass, which has a melting point of ~550°C, is commonly used as a substrate. When applying CNTs to the electron emitter sealed by soda-lime glass, it is important to lower the growth temperature to at least 550°C. Using the hot filament plasma-enhanced CVD method, the growth of CNTs was achieved at 66–66°C by Ren and his coworkers [5]. However, the growth temperature of thermal CVD is normally as high as 700–1000°C.

In this Letter, we report a low-temperature growth (500–550°C) of CNTs on a planar silicon oxide (SiO₂) substrate by thermal CVD using acetylene (C₂H₂). The cobalt–nickel (Co–Ni) catalytic particles are used as nucleation seeds for the growth of carbon nanotubes. Palladium (Pd), chromium (Cr), and platinum (Pt) are chosen as co-catalysts in order to lower the growth temperature of carbon nanotubes. Pd and Pt are the two catalysts used for most alkene hydrogenation and alkane hydroygenolysis reactions [8]. Okuyama and his coworkers showed that

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the Cr containing crystallite acts as catalyst in arc discharge synthesis of carbon nanotube [9,10].

2. Experimental section

The 20 × 30 mm size p-type silicon (100) substrate with a resistivity of 15 Ωcm was thermally oxidized. The thickness of the silicon oxide (SiO₂) layer is approximately 300 nm. The Co–Ni (Co/Ni = 1:1.5) film with a thickness of about 100 nm was thermally deposited on a SiO₂ substrate under a pressure of 10⁻⁶ Torr, followed by annealing at 400°C for 20 min. The Co–Ni film deposited on a SiO₂ substrate was dipped into a diluted aqueous HF solution for 200 s. The Pd or Cr, Pt film with a thickness of about 100 nm was thermally deposited on a SiO₂ substrate under a pressure of 10⁻⁶ Torr.

Fig. 1 is the schematic diagram for a CVD quartz reactor. The Co–Ni and co-catalyst (Pd, Cr, and Pt) films deposited on SiO₂ substrates were loaded with a face-to-face direction on a quartz boat. The face of Co–Ni and co-catalyst films deposited on SiO₂ substrates were aligned with the downward and upward directions, respectively. The distance between two films is 3 mm. Argon (Ar) was supplied to the quartz reactor in order to prevent the oxidation of metals while increasing the temperature. The metal deposited substrates were pretreated using NH₃ with a flow rate of 80 sccm, for 10 min at 850°C, which is a crucial step for the growth of carbon nanotubes [11]. After forming the catalytic particles, the carbon nanotubes were grown using C₂H₂ with a flow rate of 20–40 sccm, for 10 min at 500–550°C. Then the reactor was cooled to room temperature under ambient Ar. The carbon nanotubes were examined by a scanning electron microscope (SEM) (Philips XL30SFEG) and a transmission electron microscope (TEM) (Philips CM20T, 200 kV).

3. Results and discussion

Fig. 2a is a SEM micrograph of the carbon nanotubes grown on Co–Ni particles deposited on a SiO₂ substrate at 500°C, using Pd as a co-catalyst. The noodle-shaped carbon nanotubes with diameters distributed between 60 and 80 nm are laid down on the substrate. Without a Pd co-catalyst, no formation of carbon nanotubes on the Co–Ni particles deposited on a SiO₂ substrate at 500°C was observed. We also checked the surface morphology of Pd film deposited on a SiO₂ substrate and found no carbon nanotube growth. The result indicates that Pd plays a
role in lowering the growth temperature of carbon nanotubes on Co–Ni particles deposited on a SiO₂ substrate. It is important to mention that the carbon nanotubes are grown at the temperature below the melting point of soda-lime glass by using thermal CVD.

Fig. 2b is a SEM micrograph of the carbon nanofibers grown on Co–Ni particles deposited on a SiO₂ substrate at 550°C, using Cr co-catalyst. It shows many curled nanofibers in various diameters. Without a Cr co-catalyst, the SEM micrograph shows no carbon growth on the Co–Ni particles at 550°C. We could not find any growth of carbon nanotubes or nanofibers at 500°C, even in the presence of Cr co-catalyst. This demonstrates that Cr is a less efficient co-catalyst than Pd for the growth of carbon nanotubes.

Fig. 2c is a SEM micrograph for the Co–Ni particles deposited on a SiO₂ substrate at 550°C, using Pt as a co-catalyst. It reveals a few graphite whiskers with a diameter of a few hundred nm and nanostructured carbons. No carbon growth was found at 500°C even though Pt was used as co-catalyst. This indicates that Pt is a much less efficient co-catalyst than Pd for the carbon nanotube growth. We also observed no formation of carbon nanotubes on the Pt film deposited on a SiO₂ substrate at all.

TEM analysis was performed on the CNTs grown on Co–Ni particles deposited on a SiO₂ substrate using a Pd co-catalyst at 500°C. Following ultrasonic treatment in acetone, the peeled CNTs were dispersed on a TEM carbon microgrid. The arrow in Fig. 3a indicates a narrow inside hollow (5–10 nm) of multiwalled CNTs. Most of the closed tips are
Fig. 3. TEM images of the CNTs grown on Co–Ni particles deposited on a SiO$_2$ substrate at 500°C using Pd as a co-catalyst. (a) It shows the inside hollow with a diameter range of 5–10 nm (see arrow 1). Most of the closed tips are filled with catalytic metal particles (see arrow 2) and the roots are open due to separation from the catalytic particles (see arrow 3). It reveals a bamboo-like structure (see arrow 4) and many catalytic metal particles around the CNTs (see arrow 5). (b) A straight bamboo-shaped CNTs. (c) Wall structure of a CNT, showing waving graphite sheets and surface defects.

filled with catalytic metal particles (see arrow 2). Arrows 3 correspond to open roots separated from catalytic particles. It also reveals a bamboo-like structure in which the tube consisted of hollow compartments (see arrow 4). There are many catalytic metal particles around the CNTs, which are separated from the root of the CNTs during ultrasonic treatment, indicated by arrow 5. Fig. 3b is a magni-
fied view of CNTs, revealing their bamboo-like structure. The respective outer and inner diameters are about 30 and 6 nm. Fig. 3c is a high-resolution TEM image for the wall structure of a CNT. The outer and inner diameters are about 30 and 6 nm, respectively. The walls are composed of waving graphite sheets aligned to the tube axis. The surfaces are covered with discontinuous and/or defective graphite sheets.

The vertically well-aligned CNTs grown at the temperature range of 800–950°C usually have straight graphite sheets that are separated by 0.34 nm [12]. The waving graphite sheets and high defects on the surface could be due to a low growth temperature. Saito and Yoshikawa first reported the bamboo-like structure of CNTs grown using the arc-discharge method [13]. Recently, Wang and his coworkers have shown bamboo-shaped CNTs synthesized using the pyrolysis method [14]. The bamboo-like structure is also found in CNTs grown using microwave plasma enhanced CVD [15,16]. Li et al. have reported bamboo-shaped CNTs grown by thermal CVD using an alloy catalyst [17]. Therefore, the formation of the bamboo-like structure seems to be possible regardless of the growth method used.

Fig. 4 shows high-resolution TEM images of CNTs grown on Co–Ni particles deposited on a SiO₂ substrate at 550°C using Cr as a co-catalyst. Twisted carbon nanofibers, shown in Fig. 4a, have a diameter of about 25 nm. There are encapsulated catalytic particles (see arrow 1). The waving graphite sheets are aligned along the twisting direction as indicated.
by arrow 2. Fig. 4b shows the straight part of a twisted carbon nanofiber. The diameter is about 40 nm. The waving graphite sheets are aligned to the axis of the tube with the tilted angles shown as arrows 1, 2, and 3. Inner walls are interconnected by many conically shaped graphite bridges as indicated by arrow 4.

We have demonstrated the growth of CNTs and nanofibers on Co–Ni particles deposited on a SiO$_2$ substrate at 500–550°C using thermal CVD. Among the Pd, Cr, and Pt used as co-catalysts, Pd is found to be the most efficient catalyst for growth of CNTs. The results show that Pd, Cr, and Pt films can supply carbons for growth on the Co–Ni particles deposited on a SiO$_2$ substrate that is positioned with the face-to-face direction at a distance of 3 mm. However, the activation energy or rate constant data at 500–550°C are not known for the decomposition of a C$_2$H$_2$ molecule on the Pd, Cr, and Pt films, and thus it is difficult to explain their relative efficiency. There is a possibility that Pd (or Cr, Pt) may evaporate during the NH$_3$ pretreatment at 850°C and deposit on the Co–Ni particles deposited on a SiO$_2$ substrate. The heat of sublimation was reported to be 94, 93, and 133 kcal/mol, respectively, for Pd, Cr, and Pt [18]. Therefore, the amount of deposited metal is expected to be of the order of Pd ≈ Cr ≫ Pt. Pd and Cr deposited on the Co–Ni co-deposited SiO$_2$ substrate can provide carbon for the growth of CNTs or nanofibers. Pt may not act as an efficient catalyst because of negligible deposition. Since Okuyama et al. showed that the Cr-containing crystallite could also act as a catalyst in arc discharge synthesis of CNTs [9,10], the deposited Cr may also participate in the growth as a catalytic particle. In order to understand the experimental results, we are carrying out more experiments using these three metals.

4. Summary

In summary, we tried to grow CNTs on Co–Ni particles deposited on a SiO$_2$ substrate at 500–550°C using thermal CVD. Pd, Cr, and Pt were used as co-catalysts for decreasing the growth temperature of CNTs. Pd is found to be the most efficient co-catalyst for CNTs. Using Pd as a co-catalyst, the noodle-shaped CNTs with a diameter of 60–80 nm are grown at 500°C. With Cr as co-catalyst, curled carbon nanofibers are grown at 550°C. Using Pt as co-catalyst, graphite whiskers are grown with a low density at 550°C. CNTs grown at 500°C using Pd as co-catalyst have a bamboo-like structure, aligned waving graphite sheets, and encapsulated catalytic particles at the tip. The curled carbon nanofibers grown at 550°C using Cr as co-catalyst consist of twisted waving graphite sheets. Finally, we suggest that the use of Pd as co-catalyst is one techniques for the growth of CNTs directly on soda-lime glass substrate by using thermal CVD.

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References