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Original Article

Relatively Lower Temperature Growth of Carbon Nanotubes

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Abstract - *It is necessary to develop a synthesis method for the high-density growth of carbon nanotubes at low temperatures so that they can be commercialized in a wider range of fields. This study demonstrated the growth of pure high-density carbon nanotubes at a relatively low temperature through the thermal chemical vapor deposition growth method by modifying the conventional chemical vapor deposition system. For the system, the movement path of carbon supply gas was restricted, and gas decomposition was increased. Moreover, the reaction time between carbon feed gas and catalyst was increased, so the possibility of growing high-density carbon nanotubes was increased even at lower growth temperatures.*

Keywords - *Carbon nanotube, Chemical vapor deposition, High density, Low-temperature growth, Water vapor synthesis.*

1. Introduction

Carbon nanotubes have both metal and non-metal properties and have excellent electrical and physical properties. It is a very small nanoscale material and has superior electrical properties. The electrical behaviour of carbon nanotubes, whether metallic or semiconducting, is determined by their diameter and chirality. With its outstanding properties, it is drawing considerable research interest as a next-generation material. Carbon nanotubes comprise six carbon atoms, with hexagons connected to each other to form a tube, and have a sp^2 bond that can be seen in carbon allotropes. Carbon nanotubes exhibit diameters ranging from a few nanometers to several tens of nanometers. They can be classified into two categories. Single-walled carbon nanotubes, SWCNTs, and multi-walled carbon nanotubes, MWCNTs. SWCNTs have a wall made of a single atomic layer.

2. Literature Review

In theory, one-third of SWCNTs have electrically metallic properties, and the remainder have semiconducting properties. MWCNTs have walls made of multiple atomic layers and have the electrical properties of a metal. [1] Key techniques for synthesizing carbon nanotubes are arc discharge, chemical vapor deposition, and laser ablation. [2-4] Chemical vapor deposition, CVD, offers several advantages, including producing high-purity carbon nanotubes, promoting selective structural growth, and achieving high synthesis yields. In most cases, for the CVD process, high-temperature conditions are necessary to activate catalysts and decompose feedstock gases. However, to utilize carbon nanotubes in electronic devices such as transistors, field emission devices, and displays, a pure and low-temperature growth method is required. For example, the maximum temperature must be below 450°C to use carbon nanotubes in Complementary Metal–Oxide–Semiconductor (CMOS) interconnect technology. [5] To enhance the potential applications of carbon nanotubes in various fields, numerous studies have been conducted to lower the growth temperature of carbon nanotubes in the CVD process. Plasma-enhanced chemical vapor deposition was utilized to grow carbon nanotubes at low temperatures. [6] There have also been attempts to lower the carbon nanotubes' growth temperature using various catalysts. Carbon nanotubes were grown at low temperatures using cobalt alloy or nickel catalysts. [7, 8] Additionally, common sodium-containing compounds were used as catalysts, magnesium oxides were used as catalysts, and FeZrN catalysts were used to lower the carbon nanotube growth temperature. [9-11] Most low-temperature growth of carbon nanotubes using CVD has been conducted with horizontal tube systems. However, the flow rate of the carbon feed gas is not uniform within the tube, and especially at higher flow rates, the growth of carbon nanotubes is limited. [12] This is because of the structural characteristics of the horizontal tube, where the gas passes over the substrate with the catalyst in a short period, resulting in a short reaction time between the catalyst and the carbon. Therefore, to achieve high-purity and high-density growth of carbon nanotubes in a CVD system, it is crucial to ensure sufficient reaction time between the carbon feed gas and the catalyst.

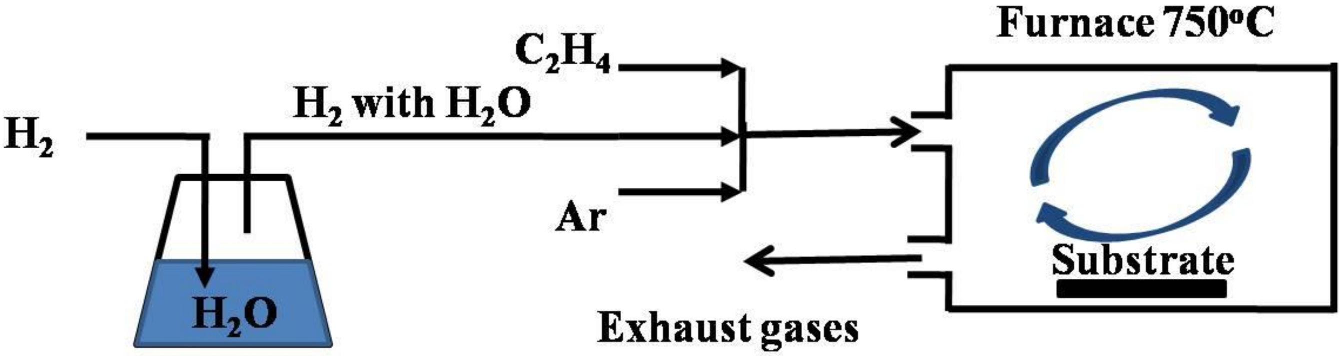

Fig. 1 Experimental methodology

This factor is important in reducing the growth temperature.This study demonstrated the growth of pure, high-density carbon nanotubes at relatively lower temperatures by modifying the thermal CVD system. In the system, the flow path of carbon supply gas was modified compared to conventional horizontal tube CVD systems to increase the reaction time between carbon feed gas and catalyst.

3. Methodology

- The quartz plate is cut into 1x1 cm pieces.
- The quartz piece is cleaned with Acetone, Methanol, and IPA and then the piece is dried by N_2 gas.
- Fe_2O_3 powder is dissolved in the solvent, Isopropyl Alcohol. The concentration of the solution is 100 *mg/ml*.
- The solution was sonicated to decompose and disperse Fe_2O_3 into small pieces for 20 mins.
- Two or three drops of the solution were applied to the quartz piece and substrate.
- The prepared substrate is moved into the one-end closed tube of the furnace.
- H2, 200 *sccm*, is injected into a water-filled flask to generate H_2 with H_2O.
- Ar, 200 *sccm*, and H_2 with H_2O gases are introduced into the one-end closed tube of the furnace.
- The temperature of the furnace is raised to 750 ^oC.
- When the temperature reaches 750 ^oC, it is waited for 5 minutes for the temperature to stabilize.
- Ar gas is stopped, and C_2H_4, 30 *sccm*, is supplied to the furnace tube for 10 mins.
- After the period, C_2H_4 is stopped, and Ar, 200 *sccm*, is supplied.
- The furnace is cooled down to room temperature, and the substrate is removed from the system.

4. Results and Discussions

Catalysts play an important role in synthesizing carbon nanotubes in thermal CVD. The catalyst size is recognized for its substantial impact on determining the diameter of carbon nanotubes and affects the crystal direction and growth direction [13]. For thermal CVD synthesis, transition metals such as Ni, Co, and Fe are generally used as catalysts, and those are deposited on a substrate. Transition metals are commonly used as catalysts because they exhibit high catalytic activity in breaking down hydrocarbons, can form metastable metal carbides, exhibit optimal bonding strength to carbon, and have a high carbon solubility limit. [14-16] In this experiment, Fe_2O_3 was used as a catalyst and dissolved in the solvent, Isopropyl Alcohol. The concentration of solution was 100 mg/ml. After that, the solution was sonicated to decompose and disperse Fe_2O_3 into small pieces. A few drops of the prepared solution were applied to the substrate, quartz. Another important factor that affects carbon nanotube synthesis is the type and flow rate of carbon supply gas. To grow carbon nanotubes at low temperatures, the carbon supply gas must be decomposed into carbon species at low temperatures. Among the gases used for carbon nanotube synthesis, acetylene (C_2H_2) or ethylene (C_2H_4) are mainly used for low-temperature synthesis, and C_2H_4 was used in this experiment. [17-18] Regarding the flow rate of the carbon supply gas, when the flow rate is increased, the wall of the carbon nanotubes can be thicker, or carbon fibers rather than carbon nanotubes can be synthesized [19-21]. In the other case, when the flow rate of the carbon supply gas was too low, the density of carbon nanotubes can be very low.

Therefore, the appropriate type and flow rate of carbon supply gas are important factors in synthesizing high-density carbon nanotubes at low temperatures. [13, 22] The flow rate of C_2H_4 in this experiment was 30 *sccm*. We found carbon fibers when the flow rate was higher. During the synthesis, hydrogen (H_2) is also required to get high-purity carbon nanotubes. Hydrogen prevents excessive decomposition of C_2H_4. Excessive decomposition of C_2H_4 results in too much carbon supply, causing the growth of amorphous carbon to mainly occur rather than the growth of carbon nanotubes [23-25]. The flowrate of H_2 was 200 *sccm* for the whole growth process. Water vapor-assisted growth of carbon nanotubes significantly improves their purity and density. The water vapor increases catalyst activity by removing amorphous carbon coating or contamination from the catalyst. If the amount of water vapor supplied is too little, the catalysts cannot be sufficiently activated.

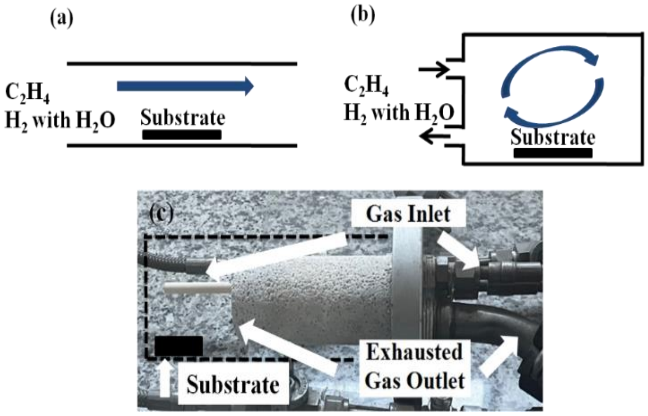

Fig. 2 Gas movement path (a) in a general horizontal tube furnace and (b) in the modified one-end closed tube furnace and the gas supply device for the tube in this experiment.

If the amount of water vapor supplied is too large, oxygen causes the materials to burn. It will be important to systematically analyze the correlation between the quantity of water vapor and the synthesis temperature and the correlation between the quantity of water vapor and the density of carbon nanotubes synthesized. In this study, water vapor was supplied by mixing H_2 before it was supplied to the furnace, and the amount of water vapor supplied was determined by the flow rate of H_2, 200 *sccm*.

For high-density growth of carbon nanotubes at low temperatures, we modified the thermal CVD system. Figure 2 shows the modified system and compares the gas movement path in a general horizontal tube furnace and the modified closed tube furnace. In a horizontal tube furnace, Figure 2 (a), the gas flow is in one direction and passes over the substrate. In the case of the one-end closed tube furnace, Figure 2 (b), the gas rotates in the tube on the substrate and can stay in the tube for a longer period. As a result, the decomposition of gas was increased, and the reaction time between carbon and catalysts was increased, so the possibility of growing high-density carbon nanotubes increased even at lower temperatures. Figure 2 (c) is an optical photograph of the gas supply device for the tube with one end closed. The gas inlet and gas outlet are installed on one side, and the dotted line represents the tube with one end closed.

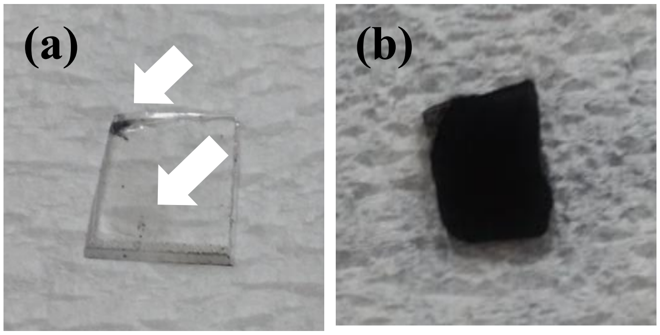

Fig. 3 Optical image of carbon nanotube synthesized (a) in the horizontal tube furnace and (b) in the modified tube furnace.

Figure 3 presents optical microscope images of carbon nanotubes synthesized. The images compare nanotubes produced in two different systems, a general horizontal tube furnace, figure 3 (a), and a modified closed tube furnace, figure 3 (b). Both synthesis processes were conducted under identical conditions, with a growth temperature maintained at 750°C and a growth duration of 10 minutes. As mentioned above, the flowrate of C_2H_4 was 30 *sccm*, and H_2 was 200 sccm. The water vapor was mixed and supplied with H_2 during the whole growth process. The comparison aims to highlight differences in the density of the carbon nanotubes resulting from the distinct growth system configurations. As can be seen in the figure, the modified system successfully synthesized high-density carbon nanotubes. This indicates that the modifications made to the furnace setup significantly improved the synthesis process. In contrast, the general horizontal tube furnace produced few carbon nanotubes across the entire substrate. In Figure 3 (a), the darker areas indicated by the white arrow are where carbon nanotubes have grown at a low density. This limited synthesis is likely due to the insufficient reaction time between the catalyst and the carbon and the limited decomposition of carbon supply gas.

Figure 4 provides an SEM image of the carbon nanotubes synthesized in the modified tube system. The SEM image shows the high density of grown carbon nanotubes.

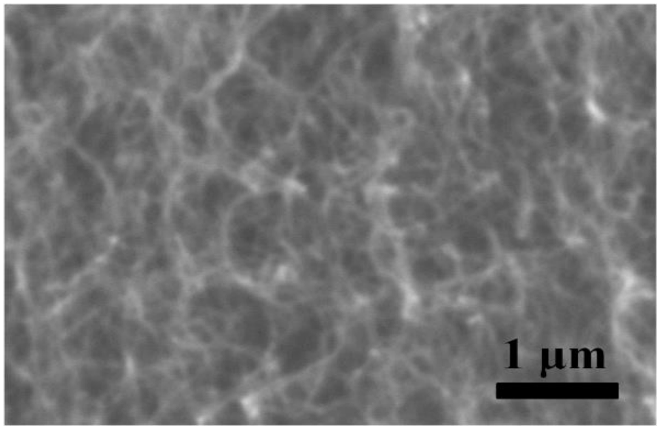

Fig. 4 SEM image of carbon nanotubes synthesized in a modified tube system

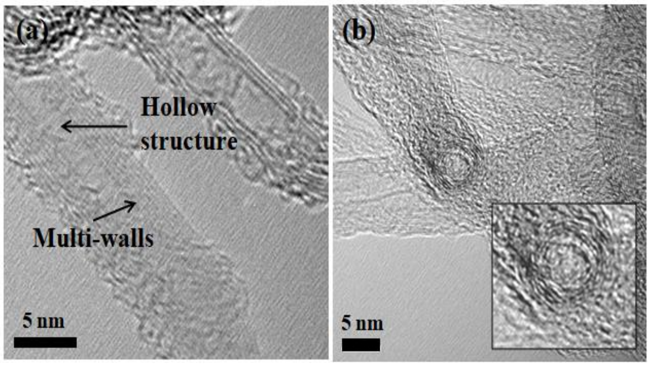

Fig. 5 TEM image of the synthesized carbon nanotubes

Figure 5 provides a TEM image of the synthesized carbon nanotubes. For TEM measurements, the grown carbon nanotubes were scraped off and dispersed in IPO, followed by sonication to prevent aggregation of the carbon nanotubes. The solution was then dropped onto a TEM grid for TEM measurement. The TEM image shows a detailed view of the nanotube′s structure, allowing for a closer examination of its morphology. MWCNTs have a hollow and cylindrical structure and multi-walls. In Figure 5 (a), the hollow structure and multiple walls are observed, and it can be strong evidence that the carbon nanotubes grown are MWCNTs. Figure 5 (b) shows a cross-section perpendicular to the cylinder's axis of the MWCNTs. The inset in the figure is a magnified view of the cross-section. It also shows the circular shape, hollow structure, and multiple walls. Typically, the top end of carbon nanotubes is closed by itself or a catalyst, so the nanotube in the figure could be cut during the scraping process from the substrate. No other substances, such as amorphous carbon, were observed in the TEM analysis.

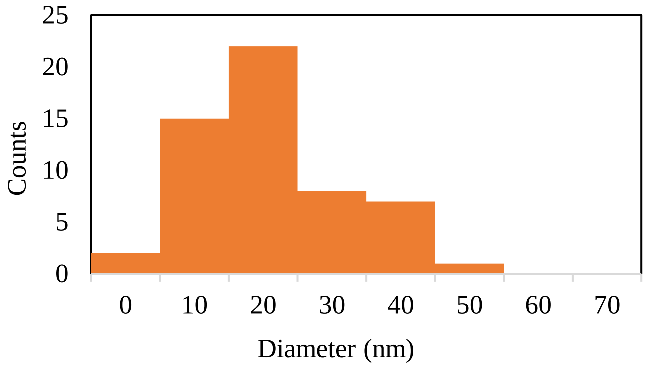

Fig. 6 Histogram of carbon nanotubes diameters

The diameter of the synthesized carbon nanotubes was measured as several tens of nanometers based on TEM analysis. This distribution of diameters suggests that the carbon nanotubes are most likely MWCNTs [24-26].

5. Conclusion

Lowering the growth temperature of carbon nanotubes is a very important issue in commercialization, especially in electronics applications. Typically, CVD growth methods for growing pure carbon nanotubes require high temperatures, so numerous studies have been conducted to lower it. In this study, the conventional CVD system with a horizontal tube was modified to a one-end closed tube CVD system to lower the growth temperature.

In the modified system, the movement path of the carbon supply gas was modified to facilitate the high-density growth of carbon nanotubes at lower temperatures compared to the horizontal tube CVD system.

High-density grown carbon nanotubes were confirmed through photographs and SEM analysis. The diameters of the grown carbon nanotubes were measured to be several tens of nanometers.

TEM analysis confirmed that the carbon nanotubes were hollow, cylindrical, and multi-walled, providing strong evidence that the grown carbon nanotubes are MWCNTs.

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