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Evaluation of the electrical properties of directly grown CNTs using thermal CVD

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Thermally-grown carbon nanotubes (CNTs) were observed with varying parameters to observe their change in shape and line resistivities. The thicknesses of the catalyst and growth temperatures were varied during CNT growth using a thermal CVD process to obtain CNTs with minimum line resistivities. It was observed that the diameter of CNTs increased as the thickness of the Ni catalyst increases at increasing growth temperatures. Moreover, the resistivity of CNTs increased with a decrease in the growth temperature, and a growth temperature of 800 °C and 10 nm of Ni catalyst are the optimal conditions for the growth of CNTs with the lowest resistivity. In this condition, the lowest resistivity was measured to be 7.48×10^{-2} Ω·cm. The line resistivity was measured from the substrate where the CNTs were grown, not that of each tube. These resistivity values are unique for use as electrodes since no vertically-grown CNTs with a thermal CVD process have had their resistivity values reported. Therefore, CNTs grown with a thermal CVD process showed their potential to be used as electrodes.

Key words: Carbon, Nanotubes, Grain growth, Sintering, Electrical properties.

Introduction

Since the discovery of carbon nanotubes (CNTs) by Ijima [1], many researches on CNTs have been made because of their unique physical properties and potential applications. In particular, the diameter, density, and structure of CNTs give rise to various chemical, physical, and mechanical properties [2-3] leading to different applications. For example, CNTs need to have a large diameter, a hollow structure, and a high metallic property for the use in fuel cells or secondary batteries, and SWNTs(single-wall nanotubes) or small diameter of vertically aligned MWNTs (multi-wall nanotubes) are desired for the use in FEDs (field-emission displays) [4]. In addition, CNTs with a low defect concentration and a high electrical conduction are desired for the use as electrodes. In particular, CNTs have comparable properties and a lower economic cost compared to that of Pt, which is commonly used for counter electrodes in DSSCs (dye-sensitized solar cells) [5]. Currently, most electrodes are made by a spin coating or spray coating method [6-10], however it was reported that directly-grown CNTs have a higher performance by minimizing the contact resistance, thus a low temperature growth for CNTs is desirable for DSSC counter electrodes. Since there has been no report about the resistivity change of directly grown CNT electrodes, studies on controlling the shape and structures of CNTs along with measurement of line resistivies, were made in this study. There are many ways of producing CNTs [11-15], and thermal CVD has been used to produce highly-purified CNTs on large areas and vertically aligned CNTs on substrates [16]. This process makes it possible to control the size and growth density of CNTs by simply adjusting the growth parameters such as the pre-treatment condition, temperature, catalyst, gas flow, and etc. For these reasons, thermal CVD is suitable for studying the growth mechanism and applications of CNTs. Moreover, the properties of CNTs are influenced by their shapes and thicknesses which can be controlled by thermal CVD.

It has been widely known that the diameter of CNTs is increased by increasing the processing temperature [17], but the relationship between catalyst thickness and CNT shapes has not been extensively studied. Therefore, in this study, the size and shape of Ni islands were observed before CNT growth, and the growth of CNTs depending on different catalyst thicknesses was studied. Also the influence of catalyst thickness was studied at temperatures ranging from 530 to 800 °C to investigate the relationship between the temperature and catalyst thicknesses. Moreover, the electrical characteristics of CNTs grown under the range of temperature stated above were studied by measuring line resistivities. Several published studies have reported electrical measurements on a statistically significant number of tube samples using atomic force microscopy(AFM) [18]. However the substrate was maintained to grow MWNTs on a large scale and their bulk resistance was measured and compared.

Experiment details

Sample preparation

SiO_2 was deposited on Si wafers to prevent the formation of the Ni silicide and different thicknesses of the Ni catalyst (3, 10, and 50 nm) were deposited on HF-cleaned Si wafers using magnetron sputtering. The samples were

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placed in the center of an alumina tube furnace and the tube was pumped down to 1.0×10^{-2} torr (1.33×10^{6} MPa).

Growth of CNTs using thermal CVD

The samples were processed at a heating rate of 5 °C·minute^{-1} in an Ar atmosphere. Annealing was carried out in an Ar atmosphere for 10 minutes at 700 °C to form randomly distributed Ni islands for the nucleation of CNTs. At growth temperatures ranging from 800 °C to 530 °C, 100 sccm of NH_3 was introduced into the tube for 10 minutes before flowing a gas mixture of H_2 and C_2H_2. The carbon source gas was introduced with the carrier gas for 20 minutes. with a ratio of C_2H_2 : H_2 = 30 sccm : 300sccm, and then slowly cooled down an Ar atmosphere.

To observe the effect of the NH_3 pre-treatment and its time dependency on the pre-treatment time, a 10 nm-sputtered Ni substrate was exposed to air to form a Ni oxide layer on the surface. Also CVD processes were carried out for 0 minute, 10 minutes, and 1 hour of NH_3 pre-treatment respectively.

After the CVD processes, the shape, diameter, and other structures were observed using FE-SEM(S-4700, Hitachi Co., Japan) and HR-TEM. (JEM-3010, JEOL Co., Japan), and their line resistivies (Ω·cm) were measured using 4-point probes (HP4145B).

Results and Discussion

The effect of growth temperature on the height of CNTs

As shown in Fig. 1, various shapes and thicknesses of the CNTs were grown at different growth temperatures and varying thicknesses of Ni catalyst.

The results of varyng the thickness of the Ni catalyst and the growth temperature are shown in Fig. 1. Generally, the diffusive flux of carbon and decompostition of the source gas through islands of the catalyst becomes faster at higher growth temperatures, resulting in long tube lengths. As shown in Fig 1(a), vertically aligned and longer CNTs were grown on the 3-nm-thick Ni catalyst compared to the CNTs on the 10-nm-thick Ni catalyst. However, as the growth temperature decreased, different shapes of CNTs with curly shapes on the top and with straight CNTs on the bottom of the CNTs film were observed as shown in Fig. 1(b). This unstable reaction was observed due to the relatively low temperature to decompose hydrocarbons at the initial stage and this explains the curly shape of CNTs on the top part. However, the bottom part resulted in a stable growth of CNTs as the carbon precursor gas is continuously supplied, resulting in straight CNTs. Therefore, it can be assumed that once the activation energy has been reached, growth of the CNTs can be easily accelerated. However, below 750, this continuous growth of CNTs becomes inhibited and all the CNTs grown below 750 °C have curly shapes as shown in Fig. 1(c) through (h).

The relationships among temperature, the height of CNTs, and the thickness of the catalyst are shown in Fig. 2. The height of the grown CNTs generally decreased as the growth temperature decreased at the same thickness of the Ni catalyst due to deactivation of the gas decomposition with decreasing temperature and a decreasing reaction rate of the nucleation of CNTs. At the same growth temperature, CNTs were grown remarkably on the thinner Ni catalyst. In particular, CNTs with a height of 60 μm were grown on a 3 nm-thick Ni catalyst at 800 °C. However, as the thickness of the catalyst was increased to 10 nm, the height of CNTs was less than 10 μm in height. Therefore, not only the growth temperature but the thickness of the catalyst plays an important role on the growth rate of the CNTs.

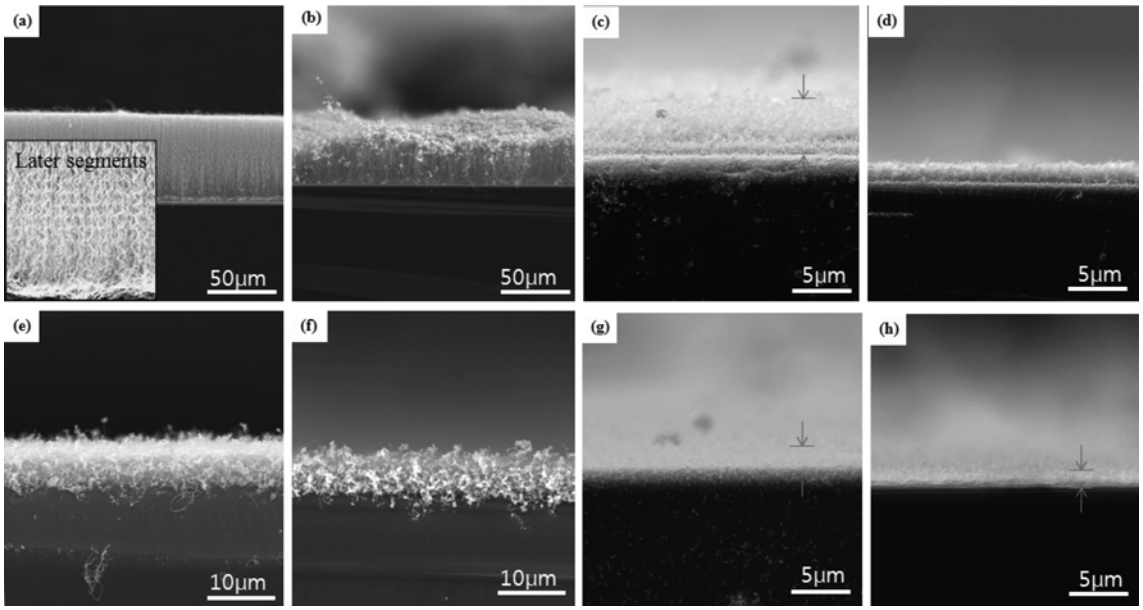

Fig. 1. SEM images of the CNTs grown at (a)-(d) 800 °C, 750 °C, 600 °C, and 530 °C, on 3 nm of catalyst, (e)-(h) 800 °C, 750 °C, 600 °C, and 530 °C, on 10 nm of catalyst, respectively.

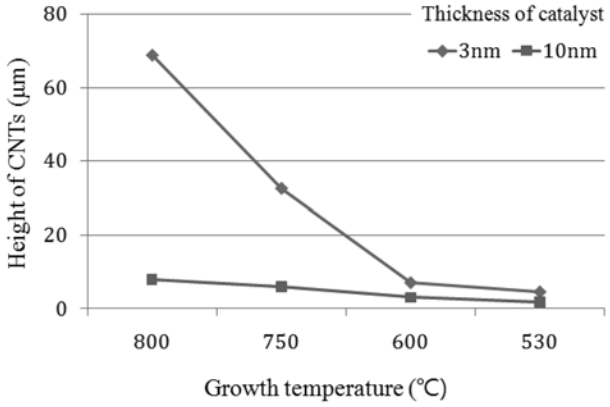

Fig. 2. Graph showing the height of CNTs at varying thicknesess of catalyst at different growth temperatures.

The relationship between the thickness of the catalyst and the diameter of CNTs.

As the thickness of the Ni layer increased from 3 to 10 nm, an average size of the Ni islands increased from 46 nm to 90 nm as shown in Fig. 3. Moreover, the diameter of the CNTs also increased from 13 nm to 31 nm, correspondingly as shown in Fig. 4. The diameter of Ni islands determines the diameter of MWNTs for thermal CVD [19]. Moreover, the height of the CNT forest decreased, resulting in a stout shape.

At a certain stage of CNT growth, the graphite covers the top of the catalyst by forming a layer of saturated carbon atoms, and the adsorption of C_2H_2 gas is stopped [20]. Therefore, it can be concluded that the alternate introduction of C_2H_2 and NH_3 gases continuously grow CNTs on small islands because of the highly activated reactions. By contrast, as the thickness of the catalyst increased, the size of the Ni islands also becomes larger, forming a stable state of the Ni crystals, and this induces a non-uniform diameter of CNTs. Moreover, increasing the size of the islands leads to the formation of CNTs with larger diameters. Therefore, as the size of the Ni crystals become large, the grains become catalytically inactive resulting in carbon layers either in the form of graphitic or amorphous CNTs, causing a thicker catalyst to form irregular carbon products.

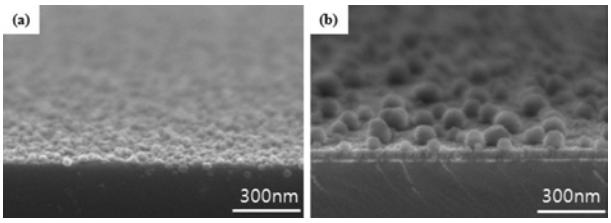

Fig. 3. SEM images of annealed Ni islands with a thickness of (a) 3 nm Ni, (b) 10 nm Ni.

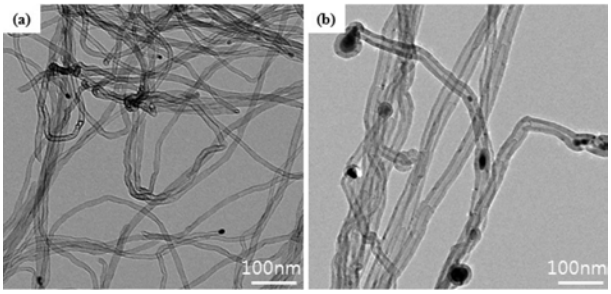

Fig. 4. TEM images of grown CNTs on (a) 3 nm and (b) 10 nm of Ni catalyst.

Comparison of line resistivities, ρ (Ω·cm)

Resistivities of CNTs grown at various conditions were measured using an I-V probe station (HP4145B) by applying a bias from −5 V to 5 V. As shown in Fig. 5, CNTs grown at 800 ºC, on 10 nm of catalyst showed the lowest resistivity, $\rho = 7.48 \times 10^{-2}$ Ω·cm, while CNTs grown at 530 ºC showed the highest resistivity, $\rho = 2.76 \times 10^{-1}$ Ω·cm. Considering the reported bulk resistivity of a CNT film to be approximately 0.1 Ω·cm [21], CNTs grown via thermal CVD showed comparable electrical properties to that of a bulk CNT film, and the highest conductivity was obtained from CNTs, which were grown at the highest temperature.

Moreover, as the thickness of catalyst becomes thicker, the resistivity slightly decreased at each temperature but the resistivity was mainly influenced by the growth temperature. As the growth temperature was increased, the yield of well-graphitized MWNTs with the highest purity increased as well, even though the CNTs grown at 800 ºC were the tallest.

Moreover, Lan *et al.* [22] reported that not only a low temperature but also a high growth temperatue close to 900-950 ºC can also cause defects. Therefore, it was found that the optimal temperature with the conditions used in these experiments is found to be at 800 ºC to grow CNTs containing the least number of defect sites on average, resulting in the lowest resistivity.

Conclusions

The resistivity, shape, and the height of CNTs grown

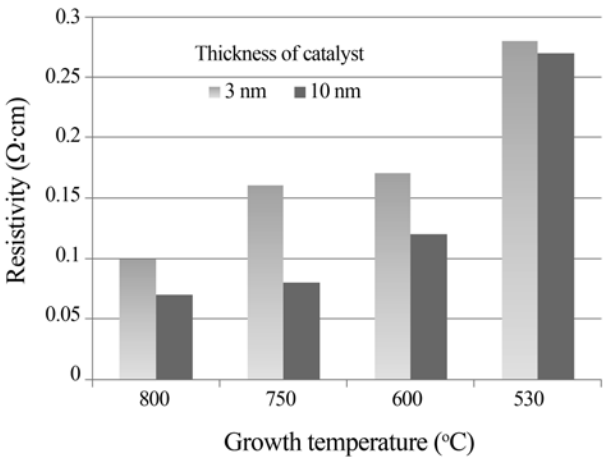

Fig. 5. Resistivity of grown CNTs with decreasing growth temperature and varying thicknesses of the catalyst.

was observed by varying the thicknesses of the Ni catalyst and the deposition temperature. As the thickness of the Ni catalyst increased, the size of the Ni islands accordingly increased making a stout shape of the CNTs. Meanwhile, the main goal of this study was to identify a favorable growth temperature and other growth conditions to obtain enhanced conductivity of CNTs, grown using thermal CVD. The resistivity results showed that CNTs with a low defects concentration and with the lowest resistivity are formed at a deposition temperature of 800 ºC. To compare with other CNT film electrodes reported previously, the line resistivity was measured to be 7.48×10^{-2} Ω·cm where MWNT and SWNT films showed of the order of ~0.1 Ω·cm and ~0.01 Ω·cm without post treatment [21]. Therefore, it is expected that the CNTs grown thermally can be potentially used for electrodes the same as coated CNT films. Overall, it was found that 10 nm of catalyst and a high growth temperature above 800 ºC are desirable for growing CNTs with a low resistivity.

Acknowledgements

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