# Low-Temperature Growth of Vertically Aligned Carbon Nanotubes for Field Emission

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## Abstract

We have investigated a low-temperature growth process of vertically aligned carbon nanotubes on a normal glass plate, which is applicable to the preparation of large-sized field emission devices. The development involves the preheating of a carbon source gas and the use of binary-layered metal catalysts. We have found that the preheating at 700°C enhances the reactivity of a carbon source gas of acetylene and contributes to the decomposition of the gas in high efficiency on the surfaces of the catalysts heated even at 450°C. For the catalysts, we have examined Fe/Al, Fe/Ti and Co/Ti. It is found that the Al base layer enhances the reaction of Fe but the Ti base layer does not. The combination of Ti base layer with Co instead of Fe is effective for growth of aligned nanotubes at a low temperature. It is also found that the precarbonization of catalysts is effective for Fe related catalysts to enhance their reaction. For Co/Ti catalysts the thickness is an important factor and thinner one is effective. The field emission properties of the low-temperature grown nanotubes have been demonstrated.

## Introduction

Carbon nanotubes (CNTs) have a high potential as a field emission electron source because of their small radii of apex and high aspect ratios.[1] They can be applied to charging devices for imaging processes in addition to cathodes of electron microscopes, flat panel displays,[2,3] cathode-ray-tube lighting elements,[4] and vacuum power switches[5] and so on. Since CNTs have a honeycomb structure with strong chemical bonds of carbon to provide long-lifetime devices, it is very significant from the global environmental point of views to realize the electron sources of CNTs. Chemical vapor deposition (CVD) processes are widely adopted to prepare CNTs, especially for vertically aligned CNT arrays. The growth temperature is typically 700°C, which is too high to be applied to the low-temperature fabrication process required for large-sized field emission devices with glass substrates (the softening point of 550°C).[6,7]

In this work, we have developed a low temperature CVD process of vertically aligned CNT arrays and examined their field emission properties.

## Experiment

The growth of vertically aligned CNTs was examined on Si substrates by thermal CVD with catalysts of binary-layered metals such as Fe/Al, Fe/Ti and Co/Ti as shown in Fig. 1. Precarbonized ones of these catalysts were also prepared by a condition of $C_2H_2$of 30 sccm diluted with He of 230 sccm at 500°C for 30min. For Co/Ti the layered films with different thicknesses of 4 nm/4 nm, 2 nm/2 nm, 1 nm/1 nm and 0.5 nm/0.5 nm were examined. In order to preheat the reaction gas, the two-zone electric furnace was used as shown in Fig. 2, where the front zone is a preheating area kept at 700°C and the rear zone is a growth area kept at a temperature ≤550°C. The temperature of the reaction gas after the front zone was estimated to be less than 200°C. The reaction gas was the same as used for the precarbonization process. The growth time is 5 minutes. We also changed the growth temperature from 450 to 550°C to investigate the temperature dependence of CNT growth. For the measurement of the field emission, the CNT array grown on a Si substrate was used as a cathode and a phosphor-coated ITO glass plate as an anode, where a gap between the two electrodes was set to be 150 μm.

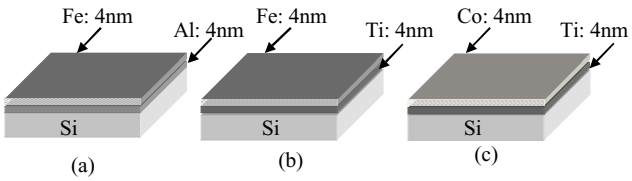


*Figure 1. Structure of examined three kinds of catalysts formed on silicon substrates.*

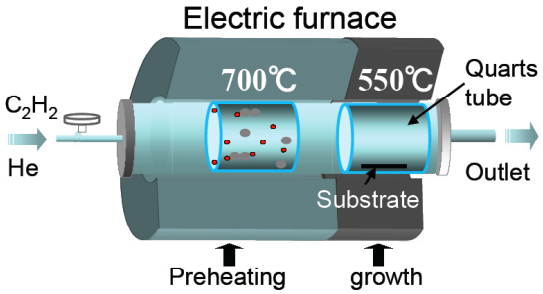


*Figure 2. Schematic diagram of apparatus for growth of vertically aligned CNTs.*

## Resuts and Discussion

### Development of Catalysts

The CVD process at 550°C using three kinds of catalysts without the preheating of the reaction gas resulted in the growth of CNTs only for Co/Ti but not for Fe/Al and Fe/Ti. However, the grown CNTs are randomly aligned. The preheating of the reaction gas, i.e. thermal excitation of molecules, effectively enhanced the reaction of $C_2H_2$ with the catalysts: CNTs were grown for the catalysts of Fe/Al, although they are randomly aligned. In the case of Co/Ti vertically aligned CNTs were grown. However, Fe/Ti did not work to grow CNTs even using the preheating gas. Figures 3(a) and 3(c) shows the scanning electron microscope (SEM) images of the CNTs grown using Fe/Al and Co/Ti with the preheating gas, respectively.

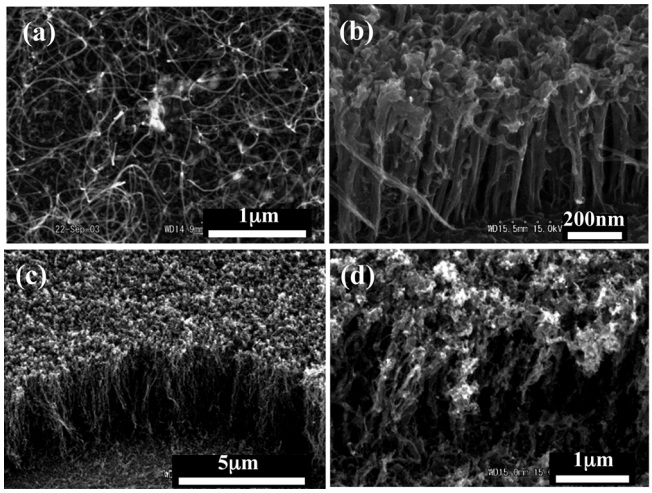


*Figure 3. SEM images of CNTs grown at 550℃ using Fe/Al catalysts ((a), (b)) and Co/Ti catalysts ((c), (d)) with ((b), (d)) and without precarbonization at 500℃ ((a), (c))*

Figure 4 shows the atomic force microscope images of three catalysts shown in Fig. 1 after the carbonization. It is clearly seen that the layered films of Fe/Al and Co/Ti change to uniformly distributed particles with the size of ~10 nm. On the other hand, the clusters with sizes of a few hundred nanometers consisting of small particles appeared for Fe/Ti. Taking into account of the fact that the particle formation from a film catalyst is essential to produce CNTs, this indicates that Fe/Al and Co/Ti work effectively but Fe/Ti does not, as is mentioned above.

For the beginning stage of CVD it is believed in general that hydrocarbon molecules are dissociated at the surface of particle catalysts and carbon atoms are absorbed into the particle catalysts and also migrate on the surface of the particle catalysts. Carbon atoms, which are fed from the supersaturated bulk of the particle catalysts or migrating on the surface of the particle catalyst, form a cap of CNT. This is the first step for the growth of CNT. At a low temperature, being supersaturated to contribute to the cap formation is time consuming, because of a low diffusion velocity of carbon atoms. The migration velocity of carbon atoms is also low, which makes the cap formation difficult. Thus the catalyst particles are covered with stacked carbon, i.e. amorphous carbon to be inactive. If carbon atoms were already included inside the catalyst and ready to contribute to the cap formation, lowering the growth temperature would be possible. Based on this consideration we applied the carbonized catalysts to the CVD process.

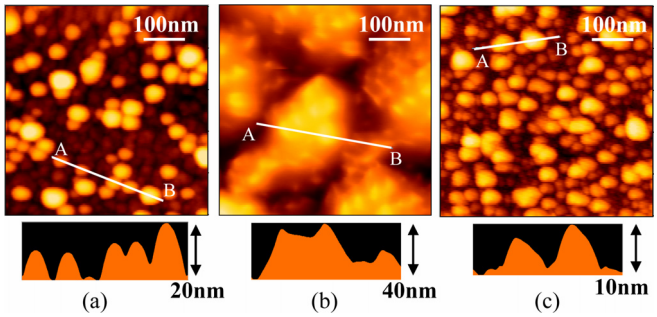


*Figure 4. AFM images of respective three kinds of catalysts illustrated in Fig. 2 after carbonization at 500℃. Lower figures show the cross section along a line A-B in the corresponding images.*

**Table I. Results of growth of vertically aligned CNTs using different catalysts with and without preheated gas and precarbonization.**

| | Fe | | Fe/Al | | Fe/Ti | | Co/Ti | | |
|---|---|---|---|---|---|---|---|---|---|
| Preheating | ● | ● | ● | ● | ● | ● | | ● | ● |
| Precarbonization | | ● | | ● | | ● | | | ● |
| CNT growth | X | Δ | X | O | - | - | X | ⊕ | Δ |

⊕ aligned, O aligned with amorphous, Δ less aligned with amorphous, X random, - no CNTs

Vertically aligned CNTs were grown for Fe/Al, although covered with amorphous carbon layer. On the other hand, in the case of Co/Ti the alignment of CNTs was degraded and in addition they were covered with amorphous carbon. These results are also shown in Fig. 4. Our consideration works well for Fe/Al but for Co/Ti. Ineffectiveness of the precarbonization for Co/Ti is not unclear. This carbonization condition might not be adequate to Co/Ti.

All of results are summarized in Table I, where the data of the conventional catalyst of Fe, which are not described in detail, are also listed as a reference. It is noted that adopting the binary-layered structure with Al increases the activity of

Fe but the combination with Ti inactivates Fe. The inactivation of Fe might be caused by its high solubility to the other metal in nanosized condition.

Based on the results that the combination of preheating the reaction gas and using binary-layered catalysts of Co/Ti is most effective for the growth of vertically aligned CNTs at a low temperature of 550°C, we investigated the dependence of the thickness of the catalyst and the growth temperature on the length and configuration of grown CNTs. Figure 5 shows the average length of vertically aligned CNTs as a function of the each layer thickness of Co/Ti. It is found that the length of CNTs increases from 4 μm to 12 μm with decreasing the thickness of Co/Ti from 2 nm/2 nm to 0.5 nm/0.5 nm. Furthermore, the CNTs have better orientation for thinner catalyst. The SEM image of the CNTs at a thickness of 0.5 nm/0.5 nm is shown in the figure. The CNTs are well oriented and also the amount of amorphous carbon is less than in the case of 4 nm/4 nm shown in Fig. 3(c).

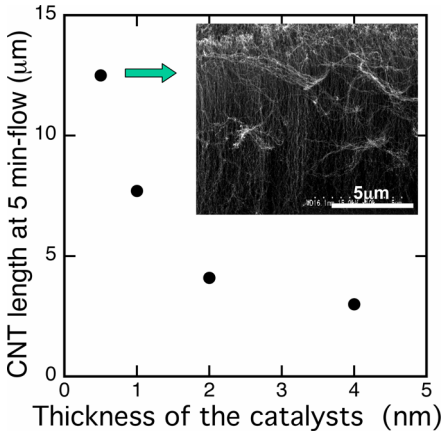


*Figure 5. Length of CNTs at 5min-source gas flow as a function of each layer thickness of the Co/Ti catalysts.*

Figure 6 shows the average length of the vertically aligned CNTs as a function of the growth temperature for Co/Ti of 0.5 nm/0.5 nm and the SEM image of CNTs grown at a temperature of 450°C. The length of CNTs decreases with lowering the growth temperature. As short as ~1 μm-long CNTs were obtained at 450°C. It is clearly seen that the orientation of the CNTs is degraded and the amount of amorphous carbon is increased as compared with the CNTs at 550°C shown in the inset of Fig. 5 and their configuration is similar to that of Fig. 3(c). These results indicate that decreasing the catalyst thickness increases the activity of the catalyst and lowering the temperature decreases it.

In order to bring the growth temperature down to 450°C with keeping a good configuration of aligned CNTs, optimization of the growth condition is still required. However, an oxidation treatment of CNTs described later practically enables us to apply the CNTs with amorphous carbon to the field emitters. In this sense the thickness of catalyst film and the growth temperature are parameters to control the length of vertical aligned CNTs.

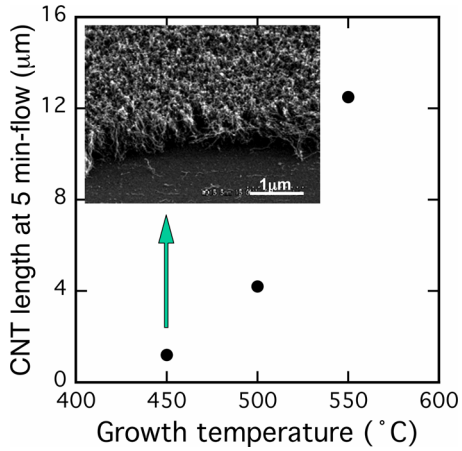


*Figure 6. Length of CNTs at 5min-source gas flow as a function of growth temperature for Co(0.5nm)/Ti(0.5nm).*

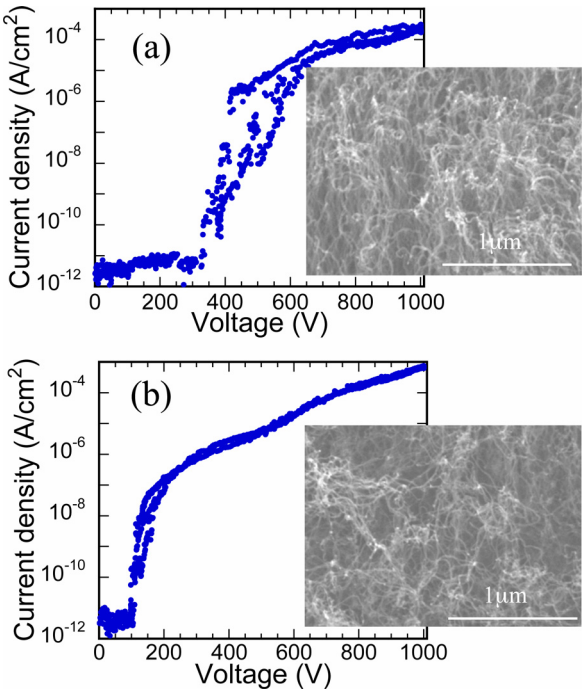


*Figure 7. I-V characteristics of field emission and SEM images of CNT arrays before (a) and after (b) the treatment at 500℃ in air for 8 min.*

**Field Emission Properties of Aligned CNTs**

Figure 7(a) shows the cyclic current-voltage characteristics of field emission for the ~5 μm-thick CNTs array grown at 550°C using Co/Ti of 0.5 nm/05 nm. As prepared CNT array shows a turn-on voltage of ~350 V. The current increases steeply with increasing the applied voltage and reaches ~ $10^{-5}$ A/cm$^2$ at 600 V. The turn-on voltage is

high as compared with the results measured for an array consisting of arc-discharge produced CNTs.[8]

In order to improve the current-voltage characteristics of the field emission, we performed the oxidation treatment of the CNT array in a condition at 500°C in atmosphere for 8 min. As shown in the inset of Fig. 7(a) where the SEM image of the surface of the as prepared CNT array is displayed, the density of CNTs is high. However, after the oxidation treatment the density decreased, which is shown in the inset of Fig. 7(b). The oxidation treatment removes amorphous components first and then pentagons usually located at the cap of CNT to close the end rather than hexagons forming a body of CNT, because the stress of the C-C bonding is higher in pentagons than in hexagon. This reduces the density of CNTs and also makes CNTs thin. The change in the surface of the CNT array is reflected to the current-voltage characteristics shown in Fig. 7(b). The turn-on voltage is reduced to ~100 V. This value is lower than that of the arc-discharge produced CNTs and comparable to that of the CNT arrays prepared at 700°C and treated by a similar manner.

## Conclusion

Vertically aligned CNTs were grown at temperatures below 550°C by the method of thermal CVD with the preheating of the reaction gas and the thin binary-layered catalyst of Co/Ti. The length of CNTs is controlled by the thickness of the catalyst and the growth temperature. The low-temperature grown CNTs showed the field emission properties comparable to the CNTs grown at 700°C.

## Acknowledgement

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## Biography

**Yoshikazu Nakayama** received his B.S. degree in Electric Engineering from Osaka Prefecture University in 1972, and a Ph.D. in Applied Physics from Osaka University in 1985. In 1972, he joined Matsushita Electric Industry Co., Ltd. where he worked on research in optical memory using holograms. In 1979, he moved to Osaka Prefecture University and was appointed to the position of professor in 1995. His work has primarily focused on nanoscience, including growth processes, nanophysics and nano-engineering of carbon nanomaterials. He is a member of the IS&T, the ISJ, the Imaging Society of Japan, the Material Research Society and the Japan Society of Applied Physics.