EFFECT OF CATALYST ON THE GROWTH OF CARBON NANOTUBES IN CVD PROCESS

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ABSTRACT

We synthesized highly aligned carbon nanotubes by thermal decomposition of acetylene gas using metal catalyst island. The alignment technique in this experiment is a very efficient method because it does not require any treatments before and after catalyst metal deposition. Alignment of nanotubes was dominated by the uniform diameter and the high density of metal catalysts. In the field emission test, the uniform emission spots on phosphor screen were obtained from the nanotubes in spite of non-aligned tube nature.

INTRODUCTION

Nanotubes have a great potential toward many electronic device applications. Especially, they have been received a considerable attention for field emitters due to their unusual structure and property. Their high aspect ratio and small tip radius enable graphitic structure to be used as emitter materials in spite of high work function.[1] However, in order to apply nanotubes to the field emitters, many actual problems should be solved, such as purification, alignment, density control, emission uniformity and stability. Among the various techniques for nanotube fabrication, such as arc discharge, laser ablation, and CVD (chemical vapor deposition) process, CVD process is the most probable technique that can solve the above problems without additional post treatment.

In CVD process for nanotube growth, metal catalysts are inevitable for the nucleation and growth process.[2-5] In addition, they play a critical role in determining the physical, chemical and electrical properties of carbon nanotubes such as its morphology, diameter, structure and conductivity. Therefore, through the control of metal catalyst, it would be possible to fabricate carbon nanotubes that showed different morphology and property.

In this work, the effect of catalyst to obtain highly aligned and uniform carbon nanotubes was investigated. In addition, in order to improve the emission uniformity, the patterned growth of nanotubes was progressed.

EXPERIMENTAL

Carbon nanotubes were grown by catalytic decomposition of acetylene in a hydrogen carrier stream over nano-sized metal particle supported on Si substrate. Two different metals, such as Co or Ni, were used as catalysts deposited with various thickness (2-10nm) by using D. C. magnetron sputtering system.

The as-deposited metal films were transformed into nano-sized particles during in-situ heating process in the CVD chamber flowing the mixture of argon and hydrogen. After the temperature reached to 800°C, acetylene mixed with hydrogen was introduced into the chamber for the growth of nanotubes. The concentration of hydrogen, which used as a carrier gas, was varied in the ratio from 0 to 0.8. The growth period was 1 hour.

To investigate the morphology of carbon nanotubes, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used. The field emission tests were performed with diode-structure, which consisted of as-grown nanotube cathode and phosphor-coated ITO (indium tin oxide) anode under ~10^{-9} Torr range.

RESULT AND DISCUSSION

To obtain the nanotubes in CVD process, metal catalyst should be prepared in the forms of nano-sized particle previously, because it acted as a seed and template of tube structure. In this work, theses nano particles were formed from thin metal film deposited on Si substrate during in-situ heating procedure up to reaction temperature required for hydrocarbon decomposition. It is a very simple way and do not require any other additional physical and chemical treatment for nano particle formation, compared to other techniques reported by CVD catalytic growth. This transformation from flat film to nanoparticles was mainly due to the difference of surface energy between metal film and substrate during high temperature heating process. Figure 1 shows the SEM image of Co and Ni catalyst particle, which was agglomerated at 800°C before acetylene gas introduction. The thickness of as-deposited film was all 2nm. As shown in Fig 1 (a), the uniform Co nano particles with 20-30nm diameter were formed and distributed with 10nm spacing over the whole substrate. On the other hand, in the case of Ni shown in Fig 1 (b), it showed somewhat variance in the diameter about 20-60nm and the 30nm spacing between the particles. The diameter of catalyst particle was determined by as-deposited film thickness. When as-deposited Co and Ni film had over 4nm thickness, the particles over 50nm diameter were formed after heating up to 800°C.

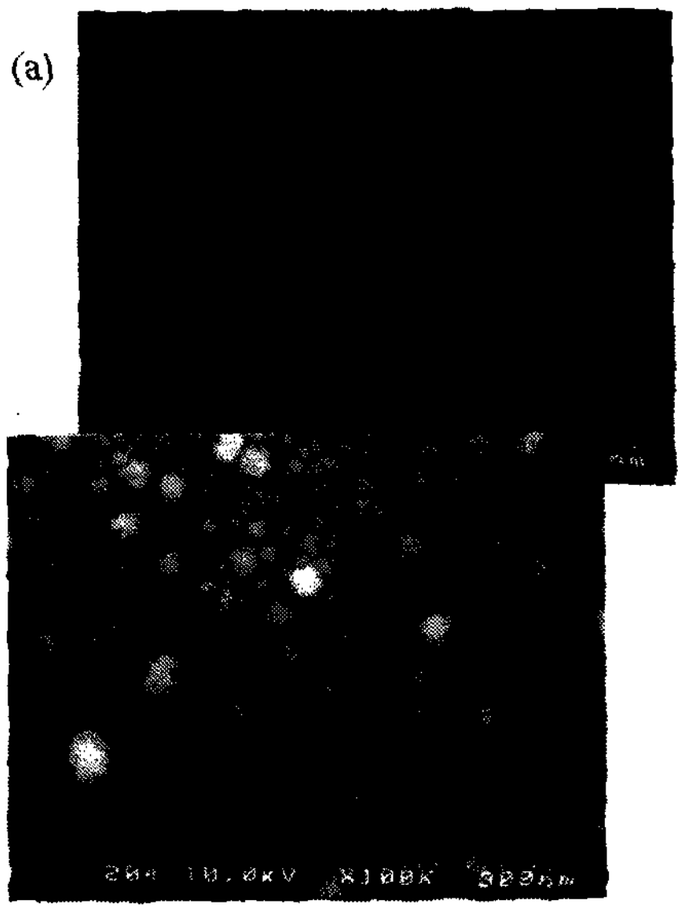

Fig. 1 SEM image of catalyst particle agglomerated at 800°C
(a) Co catalyst (b) Ni catalyst

Figure 2 (a) and (b) are the SEM image of the carbon nanotubes on the Co and Ni catalyst particles shown in Fig. 1, respectively. The carbon nanotubes were formed by the decomposition of acetylene and hydrogen gas mixed with 3:7 ratios at 800°C for 1 hour. As shown in Fig. 2 (a), the whole surface was covered with highly aligned carbon nanotubes perpendicular to the substrate on Co catalyst. They were quiet uniform in length about 13mm height and densely packed. It was observed that the nanotubes had about 20-30nm diameter and 10nm spacing. On the other hand, the tubes grown on Ni catalyst particles were not aligned and showed the crooked tube structure. This result might be due to the difference in density and distribution of the metal catalyst. Therefore, it can be concluded that the alignment of nanotubes depends on the nature of catalyst particles, such as uniform diameter and high density. In addition, the growth condition of nanotubes was very restricted in the reaction temperature, and the ratio of hydrocarbon gas. The composition of amorphous carbon in the film increased at low temperature (below 600°C) and high ratio of hydrocarbon gas. In addition, the film was not covered by nanotubes but amorphous carbon on the particles over 50nm diameter.

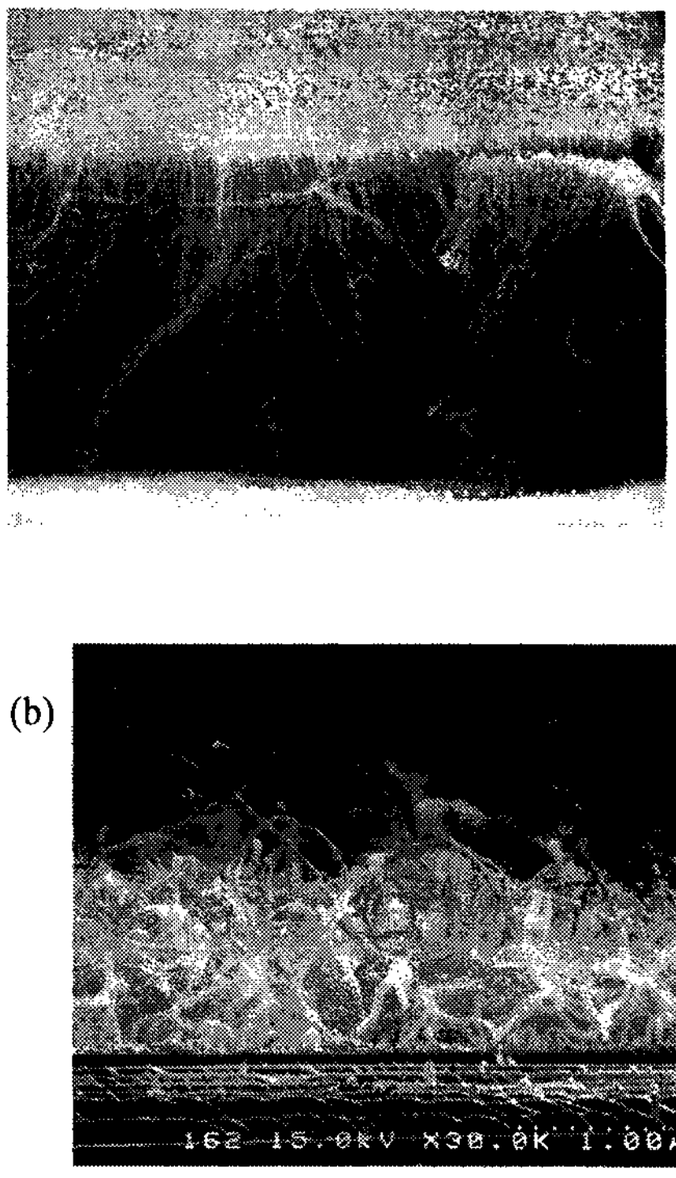

Fig. 2 SEM imagesof carbon nanotubes grown on Co catalyst (a) and Ni catalyst (b) at the temperature of 800°C

For the field emission test, the nanotube cathode was grounded (0V) and the phosphor-coated ITO anode was positively biased up to 10V/μm. In the I-V tests of two samples above mentioned in Fig. 2, the emission current showed almost same values. The turn on field was 3.5V/μm and the field, required 0.1mA/cm^2, was about 8V/μm. However, the emission current for the aligned natotubes on Co catalyst could not be considered, because the emission pattern on phosphor screen indicated that it was mainly originated from the edge of samples. Namely, the electric field cannot be induced to the nanotubes because of narrow spacing between the tubes due to their high density. However, for the nanotubes on Ni catalyst shown in Fig. 3, the uniform emission spots from 1cm x 1cm sample were observed overall surface at the field of 8V/μm in spite of their crooked morphology, compared to aligned nanotubes. It means that the not-aligned nanotubes could be used as a field emitter, if emission

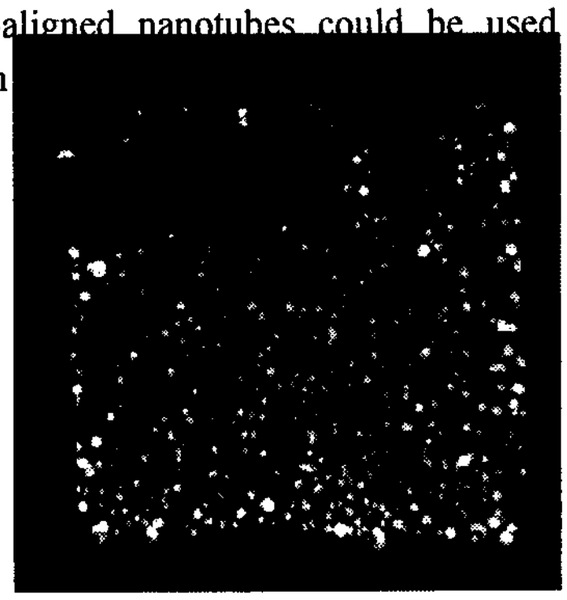

Fig.3 Emission pattern of carbon nanotubes on Ni catalyst at 0.1mA current

To obtain the uniform emission from aligned nanotubes with high density, the patterned growth of nanotubes should be achieved.

CONCLUSION

Carbon nanotubes were produced by thermal decomposition of acetylene gas using metal catalyst. The aligned nanotubes on Co catalyst showed about 20nm in diameter and 13μm in length, respectively. This alignment was achieved by the uniform diameter and high density of metal catalyst, agglomerated by in-situ heating process at the CVD reaction temperature of 800°C. The nanotubes on Ni catalyst showed uniform emission properties on phosphor screen in spite of their crooked and not-aligned tube nature.

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