Synthesis and field emission of double-walled carbon nanotubes

S. H. Lee, S. I. Jung, T. J. Lee, , W. S. Kim, J. H. Cho, H. J. Kang, G. M. Kwon, C. J. Park, S. H. Seo, K. Y. Jeon, B. Ha, C. J. Lee*

Division of Electrical and Computer Engineering and Department of Nanotechnology, Hanyang University, 133-791 Seoul, Korea

Abstract

We have investigated the synthesis and field emission properties of high-quality double-walled carbon nanotubes (DWCNTs) using a catalytic chemical vapor deposition method and a hydrogen arc discharge method. The produced carbon materials using a catalytic CVD method indicated high-purity DWCNT bundles free of amorphous carbon covering on the surface. By adopting a hydrogen arc discharge method, we could obtained high-purity DWCNTs in large-scale. DWCNTs showed low turn-on voltage and higher emission stability compared with SWCNTs

1. Introduction

The CNTs have lower emission turn-on fields and larger emission current densities than other emitter materials [1-5]. Recently, much attention has been attracted to the synthesis of double-walled carbon nanotubes (DWCNTs), which consist of two concentric cylindrical graphene layers. DWCNT has some advantages on field emission over other types of CNTs such as single-walled carbon nanotube (SWNT) and multiwalled carbon nanotube (MWNT). Here, we demonstrate the synthesis of high-purity DWCNTs by catalytic decomposition of carbon containing sources over Fe-Mo / Al_2O_3 or MgO catalyst, and a hydrogen arc discharge. We also investigate field emission properties such as turn-on field, current density, and current stability from DWCNTs.

2. Experimental

2.1 Synthesis of DWCNTs by a catalytic CVD

For the synthesis of DWCNTs, the Fe-Mo/MgO catalyst was produced by an impregnation method. ~200mg of supported Fe-Mo catalyst was placed into a quartz boat at the center of the reactor tube. The quartz tube then was heated up to 900 °C in an Ar atmosphere. Subsequently, to synthesize DWCNTs, carbon source and carrier gases (Ar 500 sccm/H_2 200 sccm) were introduced into the reactor maintained at 900 °C for 10 min.

2.2 Synthesis of DWCNTs by arc discharge

High-purity DWCNTs were synthesized by a conventional dc arc-discharge method in a stainless steel chamber. The anode was a graphite rod with a drilled hole (3 mm in diameter) filled with the mixture of Fe metal catalysts, graphite powder and FeS promoters. The amount of Fe catalysts with respect to graphite powder was fixed while the amount of FeS promoters with respect to Fe catalysts was varied to 100, 50, 20, 10 (wt %). Arc evaporation was maintained for 20 min in an atmosphere of H_2 of 300-700 Torr. The discharge current was also used in the range of 30 to 70 A. The soot material was collected on the cathode and the chamber walls. The web-like material was obtained around the cathode after the arc evaporation.

2.3 Preparation of DWCNTs

The as-grown DWCNTs were purified with acid treatment to remove catalyst such as Fe-Mo/MgO, Fe, FeS. The purified DWCNTs were dispersed in alcohol by an ultra-sonication and then introduced on the Ti deposited silicon (Si) substrate by a spray method [6, 7]. The CNT emitters deposited on the Ti/Si substrate were annealed with Ar/H_2 mixture gas at 400 °C for 20 min using rapid thermal annealing. Field emission measurements were prepared at room temperature in a vacuum chamber with a ~$1x10^{-7}$ Torr. The measured field emitting area was 7.0 mm^2. Al_2O_3 thin mask (thick = 110 um) was introduced to avoid the edge emission from the Si substrate. The distance between the DWCNT emitters and the Cu anode plate was 300 um. Emission current was measured using a keithley 6517A electrometer and recorded at 1.0 sec intervals.

3. Results and discussion

Figure 1(a) show the SEM image of the as-synthesized DWCNTs produced by catalytic decomposition of CH_4 over Fe-Mo/MgO catalyst at 900 °C, respectively. High-purity DWCNTs are produced by a catalytic chemical vapor deposition method as shown in Figure 1(a). The HRTEM image of DWCNT before purification indicates clear two graphene layers as shown in Figure 1(b).

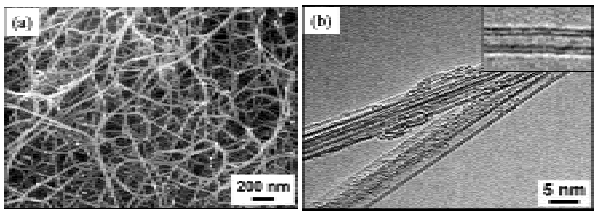

Figure 1. (a) SEM image and (b) TEM image of the as-synthesized DWCNTs by a catalytic decomposition of CH_4 over Fe-Mo/MgO catalyst at 900 °C.

Figure 2(a) show the SEM image of the as-synthesized DWCNTs produced by a hydrogen arc discharge method. Some catalyst particles(white spots) appear on the surface of DWCNTs even though the produced DWCNTs indicate high purity. Figure 2(b) show the HRTEM image of the as-synthesized DWCNTs produced by a hydrogen arc discharge method, indicating two graphene layers. Especially the DWCNTs by arc discharge have larger diameter compared with DWCNTs by a catalytic decomposition of CH_4. From HRTEM observation, we understand that DWCNTs by a catalytic decomposition of CH_4 have smaller diameter than that of DWCNTs by arc discharge.

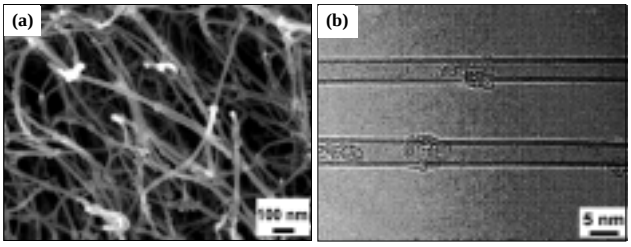

Figure 2. (a) SEM image and (b) TEM image of the as-synthesized DWCNTs by a hydrogen arc discharge method.

Figure 3 shows the field emission characteristics from DWCNT emitters measured at simple diode structure with DC bias voltage. DWCNTs by CCVD indicate the low turn-on electric field about 1.7 V/μm at ~ 1.0 x 10^{-7} mA/cm^2 and the high emission current density about ~ 2.05 mA/cm^2 at the applied electric field of 3.6 V/μm as shown in Figure 3(1). On the other hand, DWCNTs produced by a hydrogen arc discharge method show the relatively high turn-on electric field was about 2.8V/μm at ~ 1.0 x 10^{-7} mA/cm^2 and the lower emission current density about ~ 2.4 mA/cm^2 at the applied electric field of 6 V/μm compared with DWCNTs produced by a catalytic decomposition of CH_4.

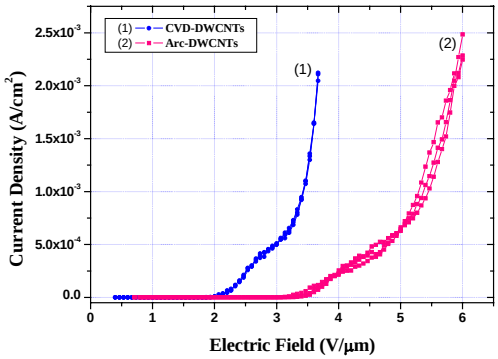

Figure 3. Field emission characteristics from DWCNTs at a diode structure with a DC bias voltage. (1) field emission from DWCNTs by a catalytic decomposition of CH_4 and (2) field emission DWCNTs by arc discharge.

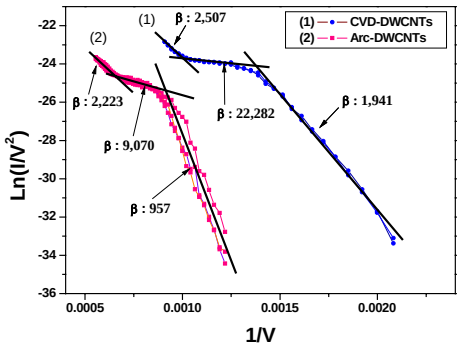

Figure 4. Fowler-Nordheim plots from DWCNTs. (1) DWCNTs by CCVD and (2) DWCNTs by arc discharge

Figure 4 shows the Fowler-Nordheim (F-N) plot from DWCNTs. In this work, F-N plot indicates linear, indicating vacuum tunneling from DWCNT tips. DWCNT emitter by CCVD show higher field enhancement factor (β) compared with DWCNTs produced by arc discharge. It is considered that the higher field enhancement factor (β) in DWCNTs by CCVD is caused by smaller diameter of DWCNTs compared with DWCNTs by arc discharge.

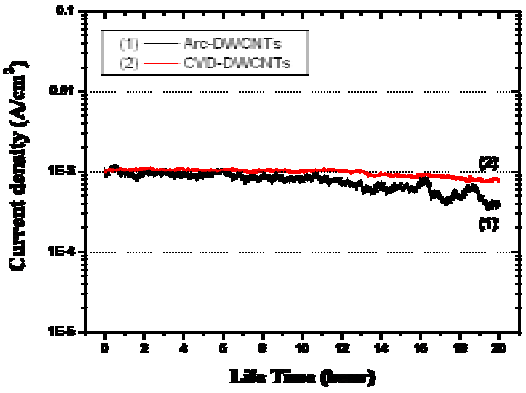

Figure 5. Field emission reliability from DWCNTs during lifetime measurement at a diode structure with a constant DC bias voltage. (1) DWCNTs by arc discharge and (2) DWCNTs by CCVD.

Figure 5 shows lifetime properties of field emission from DWCNTs with a constant DC bias voltage for 20 hours. DWCNTs by CCVD indicate fairly good reliability at high current density for 20 hours. On the other hand, DWCNTs by arc discharge reveal relatively poor reliability compared with DWCNTs by CCVD. We consider that emission reliability is mainly dependent on diameter of DWCNTs because crystallinity of DWCNTs by arc discharge show higher than that of DWCNTs by CCVD according to TGA. Here, we understand that DWCNTs have better emission stability than other reported SWCNTs [8, 9].

4 Conclusion

We have synthesized high-purity DWCNTs and investigated field emission properties from DWCNTs. DWCNTs revealed low turn-on voltage similar to SWCNTs but they showed better emission stability than that of SWCNTs. According to our results, emission properties are largely dependent on diameter of DWCNTs.

5. References

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