

Available online at www.sciencedirect.com



solid state communications

Solid State Communications 144 (2007) 498-502

www.elsevier.com/locate/ssc

Synthesis of MWNTs using Fe–Mo bimetallic catalyst by CVD method for field emission application

B.K. Singh^{a,*}, Sung-Wook Cho^a, K.S. Bartwal^b, Nguyen Duc Hoa^c, Hojin Ryu^b

^a Minerals & Materials Processing Research Division, Korea Institute of Geoscience & Mineral Resources, Gajeong-dong 30, Yuseong-gu, Daeieon 305-350. South Korea

^b Advanced Materials Division, Korea Research Institute of Chemical Technology, P.O. Box 107, Yuseong, Daejeon 305-600, South Korea ^c Department of Materials Science and Engineering, Chungnam National University, 220 Gung-dong, Yuseong, Daejeon 305-764, South Korea

> Received 13 February 2007; received in revised form 27 June 2007; accepted 16 August 2007 by T. Ando Available online 23 August 2007

Abstract

Multiwalled carbon nanotubes (MWNTs) were synthesized by chemical vapor deposition technique using MgO supported bimetallic Fe–Mo catalyst. The role of Mo on the quality of as-synthesized CNTs and their application in field emission has been investigated. The field emission properties of the device fabricated from the CNTs synthesized with Fe–Mo catalyst was found to be better than the similar device prepared with CNTs synthesized with Fe and the transfer of the device fabricated state.

© 2007 Elsevier Ltd. All rights reserved.

PACS: 81.07.De; 81.16.Hc; 68.55.Jk

Keywords: A. Carbon nanotubes; B. Chemical vapor deposition; D. Raman spectroscopy; D. Field emission

1. Introduction

Carbon nanotubes (CNTs) are interesting materials in view of their wide range of applications in hydrogen storage, chemical sensor, catalytic support, biochemical applications and field emission [1]. Such tremendous applications are due to unique geometry, high chemical stability, high mechanical strength and excellent thermal and electrical conductivity [2,3]. Specifically, for applications related to field emission device, the small size and sharp tip morphology of carbon nanotubes is useful as it can act as an electron gun. The electrons emitted from the carbon nanotubes can be used in flash memories, electron microscopy, X-ray tubes, light-sources and field emission display devices. However, for the practical application it is crucial to achieve economical mass production of CNTs of right morphology. In recent years, commercial field emission displays [4] are being synthesized by low-cost screen-printing technique. As far the synthesis of CNTs is

concerned, various synthetic methods e.g. arc discharge [5], laser ablation [6], plasma enhanced chemical vapor deposition (PECVD) [7] and chemical vapor deposition (CVD) [8] are currently practiced. Among these methods, CVD is one of the most commonly used techniques for laboratory and commercial scale synthesis of CNTs. Using the CVD method, CNTs can either be grown by the floating catalyst method [9,10] or over catalysts deposited on solid supports [11,12]. In both the cases, transition metal catalyst nanoparticles are considered to be the nuclei and potential sites for the growth of CNTs at moderate temperatures [13]. Individually Fe, Co and Ni were commonly employed for the formation of CNTs by chemical vapor deposition technique; however, bimetallic catalysts like Fe-Mo [14,15], Co-Mo [16,17] Co-Ni [18] and Fe-Co [19,20] have also been effectively utilized. Also, the use of the solid support to the active catalyst has a detrimental effect on the yield, morphology and purity of the CNTs produced. Various solid supports such as alumina [21], zeolite [22], silicas [23] and MgO [24] with different hydrocarbons viz., CO, ethane, methane, acetylene etc., as carbon source have been investigated.

^{*} Corresponding author. Tel.: +82 42 868 3606; fax: +82 42 861 9727. *E-mail address:* bks_he@yahoo.co.in (B.K. Singh).

In the present work, we describe the synthesis of CNTs over Fe- and Mo-based bimetallic catalytic system on MgO support using acetylene (C_2H_2) as a carbon source. We have also investigated the efficacy of the as-synthesized CNTs for their application in the field emission device fabricated by screen-printing method. The effect of transition metal ions Fe and Mo individually and in combination for the synthesis of CNTs and the consequent field emission devices has also been investigated.

2. Experimental details

2.1. Preparation of carbon nanotubes

The carbon nanotubes were synthesized by Chemical Vapor Deposition (CVD) method using MgO/Fe-Mo as catalyst and C₂H₂ gas as a carbon source. The use of MgO was reported to be particularly advantageous in terms of ease in the purification step of as-formed CNTs due to the high solubility of MgO in dilute hydrochloric acid that does not damage the CNTs produced [25]. Different metal ion compositions were supported on MgO keeping the support to metal ratio 1:1. We prepared seven catalysts with a general molecular formula of MgOFe_xMo_y where the values of x and y were varied from 0 to 1.0 i.e. MgOFe_{0.0}Mo_{1.0}, MgOFe_{0.5}Mo_{0.5}, MgOFe_{0.6}Mo_{0.4}, MgOFe_{0.7}Mo_{0.3}, MgOFe_{0.8}Mo_{0.2}, MgOFe_{0.9}Mo_{0.1} and MgOFe_{1.0}Mo_{0.0}. Here we describe the method for the synthesis of CNTs with catalyst composition MgOFe_{0.6}Mo_{0.4} as a representative synthesis method. The same procedure with variations in ingredients composition was followed for the synthesis of CNTs with other catalyst composition. In a typical synthesis of CNTs, analytical grade Fe(NO₃)₂·9H₂O (2.1720 g, 0.005 mol), (NH₄)₆Mo₄O₂₄ (2.5774 g, 0.002 mol), and Mg(OH)₂ (0.7233 g, 0.012 mol) were mixed with ethanol (4 ml) in an agate mortar and the slurry was grounded well during which the ethanol got evaporated. All operations were carried out in an efficient fume hood. The resulting powder was dried in an oven at 100 °C for 10 h and grounded again in an agate mortar. The fine powder (0.1 g) thus obtained was then uniformly spread in an alumina boat and was placed in the central region of a horizontal 100 cm long quartz tube furnace having an inner diameter of 4.5 cm. The furnace was flushed with argon gas while it was heated at a rate of 10 °C/min till it attained 800 °C. After the attainment of the desired temperature, H₂ gas was introduced into the furnace at a flow rate of 100 cc/min for 60 min so as to generate active metallic (Fe, Mo) or bimetallic (Fe-Mo) nanoparticles on MgO support. Subsequently, C₂H₂ gas in different quantities varying from 10 to 50 cc/min was introduced into the furnace for 1 h maintaining the flow of H_2 gas constant. We optimized the condition and the maximum yield (0.4 gm) of CNTs at C2H2 flow was obtained at 15 cc/min.

The morphology and microstructure of as-synthesized carbon materials were characterized by scanning electron microscopy (Philips XL 30S), high-resolution transmission electron microscopy (HRTEM, Techni GII, FEI 20), EDS (JMS-6700 F) and FT-Raman spectra were recorded under



Fig. 1. Schematic diagram of the emission testing circuit for MWNTs vacuum diode.

ambient conditions using a Brüker FRA-106/S with the excitation laser source of Nd:YAG (wavelength: 1.064 μ m) remaining constant and with an optical power of 100 mV at the sample position.

2.2. Fabrication of field emission device

Fig. 1 shows the schematic diagram of the diode-type field emitter. The field emitter device was fabricated by an inexpensive and simple screen-printing method. The mixture of 100 mg purified CNT powder synthesized with different compositions of catalyst MgOFe_{1.0}Mo_{0.0}, MgOFe_{0.9}Mo_{0.1}, MgOFe_{0.7}Mo_{0.3}, MgOFe_{0.6}Mo_{0.4}, 20 ml of organic vehicle (Trepineol dihydro) and 100 mg of organic binder (Ethylcellulose) were premixed through solder paste softener for 10 min. We denoted S1, S2, S3, and S4 for devices which were fabricated using CNT powders synthesized with composition of catalyst MgOFe_{1.0}Mo_{0.0}, MgOFe_{0.9}Mo_{0.1}, MgOFe_{0.7}Mo_{0.3}, MgOFe_{0.6}Mo_{0.4}, respectively. After mixing the CNT with organic vehicle and organic binder, the three-roll mill process was carried out for mixing and dispersion of CNT powders in organic vehicle as polymer matrix. The well-dispersed CNT paste was then printed onto an indium tin oxide ITO/Glass substrate using the printing-mask with 2×2 cm in size. After that the samples were dried on a hot plate at 100 °C for 30 min to obtain the uniform thickness of CNT paste films. The residue of the organic vehicle and binder in the paste were removed in order to obtain the stable emission characteristics by annealing the CNT paste films at 400 °C in air for 1 h. The field emission properties of diode-type emitter were characterized in the vacuum chamber of 10^{-6} Torr. The spacer has a thickness of $\sim 150 \,\mu\text{m}$, the anode is phosphor/glass. The data (I–V) was automatically recorded by using a programmable software (Keithley model 248 high voltage supply).

3. Results and discussion

The morphology of the as-synthesized carbon nanostructures was investigated by scanning electron microscopy (SEM) images. Fig. 2 shows the SEM image of the sample gown with MgOFe_{0.0}Mo_{1.0} as catalyst. It is evident from the figure that there are no fibrous structures present in the sample. The absence of any CNT-like structure suggests that Mo itself is not suitable as catalyst for the growth of CNTs [26].

The SEM image of the sample grown with $MgOFe_{1.0}Mo_{0.0}$ as catalyst is shown in Fig. 3(a). Though the sample shows



Fig. 2. SEM image of sample obtained using the $MgOFe_{0.0}M_{1.0}$ catalyst.



Fig. 3. (a) SEM image of the CNTs grown over $MgOFe_{1.0}Mo_{0.0}$ catalyst, (b) HRTEM images of MWNTs of (a) at low and high magnification (inset).

CNT-like structure, the presence of different sizes of CNTs together with the agglomeration of amorphous carbon and catalyst indicates uneven dispersion of the active catalyst. The TEM micrograph of MgOFe_{1.0}Mo_{0.0} is shown in Fig. 3(b). The TEM image of this sample confirms the presence of carbon



Fig. 4. (a) SEM image of the CNTs grown over $MgOFe_{0.9}Mo_{0.1}$ catalyst (b) HRTEM image of MWNTs.

nanofibers embedded with uneven sized lumps of catalyst and carbon nanotubes. The carbon nanofibers have large diameter of 72 nm with no hollow core when the carbon nanotubes have smaller outer diameter of about 20 nm (Fig. 3(b) inset). The CNTs appear to be multiwalled carbon nanotubes with the wall thickness of about 5 nm. The interplanar distance between two graphite layers is estimated to be about 0.345 nm, which is higher than the value reported for the graphite phase (0.335).

In the SEM image of the sample grown with MgOFe_{0.9}Mo_{0.1} (bimetallic) catalyst (Fig. 4(a)), we see the presence of smooth, fairly uniform and continuous carbon nanotubes with a length running to several micrometers. The presence of the catalyst at the tips of the CNTs can also be clearly seen in its HRTEM images (Fig. 4(b)). The EDS of this sample (not show here) clearly indicates the presence of both Fe and Mo. Also the size of the catalyst crystallite seems to be fairly uniform.

Morphological features observed for the samples grown individually with Mo and Fe and with Fe–Mo were analyzed. It is to be noted that Mo by itself is not favourable for the growth of CNTs but helps in the dispersion of the Fe catalyst which is responsible for the uniform growth of CNTs in the case of Fe–Mo catalyst.

In order to optimize the maximum yield of CNTs by changing the composition of the catalyst, CNTs yield was calculated by weighing the sample using the following



Fig. 5. The yield of CNTs (%) as a function of Mo catalyst loading during the 60 min growth time with a flow of $H_2 + C_2H_2$ (100 + 15 cc/min).

equation:

 CNT_S yield (wt.%) = $[(M_F - M_1)/M_1] \times 100$,

where M_F is the total weight obtained after synthesis and M_1 is the initial weight of the powder after reduction. Fig. 5 clearly demonstrates that the maximum yield of the CNTs was obtained with the catalyst composition, $MgOFe_{0.9}Mo_{0.1}$. With the use of 0.1 g of bimetallic catalyst, up to 0.4 g CNTs were synthesized which is better than the yields obtained with other catalyst compositions. Raman spectroscopy was employed to characterize the quality and crystallinity of the as-synthesized MWNTs using Fe-Mo and Fe on MgO support as catalyst (Fig. 6). Both the Raman spectra show two strong peaks at 1300 cm^{-1} and 1600 cm^{-1} , which correspond to the peaks of multiwalled carbon nanotubes [27]. The former band corresponds to the defect-induced Raman band and is known as the defect mode, A_{1g} - or D-band associated with the disordered graphite- or diamond-like carbon. The latter peak, referred to as G-band, represents the Raman-allowed E_{2g2} mode of graphite and is related to the vibration of C-C bonded in a two-dimensional hexagonal lattice of graphite layer [10]. The ratio of the intensities of the two bands is a reflection of the quality of the synthesized material. The I_D/I_G ratio for the MWNTs grown with MgOFe_{0.9}Mo_{0.1} was found to be 1.15 (Fig. 6(a)) which indicates the presence of relatively better quality CNTs in this sample as compared to MWNTs grown with MgOFe_{1.0}Mo_{0.0} (Fig. 6(b)) for which I_D/I_G ratio was about 1.37. This observation also indicates that by adding small amounts of Mo on the Fe catalyst it is possible to increase the quality of the CNTs. However, the presence of D-peaks as compared to G-peaks in both the samples shows that CNTs still possess some amount of defects and impurities.

The synthesized carbon nanotubes were used to fabricate the field emission diode structure. For the comparison of the effect of the quality of the CNTs on the field emission property, the emission diode structures were prepared from the CNTs grown with the catalysts MgOFe_{1.0}Mo_{0.0}, MgOFe_{0.9}Mo_{0.1}, MgOFe_{0.7}Mo_{0.3}, MgOFe_{0.6}Mo_{0.4}, denoted as S1, S2, S3, and S4 for devices which were fabricated using CNT powders



Fig. 6. Raman spectra of the as-synthesized MWNTs by catalytic decomposition of acetylene over (a) $MgOFe_{0.9}Mo_{0.1}$ and (b) $MgOFe_{1.0}Mo_{0.0}$.



Fig. 7. Field emission behaviour of the CNTs, inset is the corresponding F–N plots of the data.

synthesized with composition of catalyst, respectively. Fig. 7 shows the J–V characteristics of the fabricated diode emitters. The turn-on electric field of the CNT-based emitter (defined as the electric field at $10 \ \mu\text{A/cm}^2$) is the smallest for sample S2 of 2 V/µm and about 3 V/µm for others. The smaller turn-on field is expected due to the smaller nanotubes. The maximum current density of sample S1 is 0.52 mA/cm², it is lower than that of sample S2 (1.16 mA/cm²), S3 (0.64 mA/cm²), and S4 (0.62 mA/cm²). The inset in Fig. 7 is the Fowler–Nordheim (F–N) plots of the emission properties. The F–N equation can be written as [28]:

$$I = J \times \alpha = A \times V^2 \exp(-B/V) ,$$

where $A = 1.42 \times 10^{-6} \times \alpha \times \beta^2 / \Phi \times \exp(10.4/\Phi^{1/2})$
and $B = 6.44 \times 10^7 \times \Phi^{3/2}/\beta$.

By using the work function of CNTs $\Phi = 4 \text{ eV}$, the calculated value for the field enhancement factor β is 17.17×10^4 , 19.75×10^4 , 18.81×10^4 and 16.94×10^4 for samples S1, S2, S3, and S4, respectively. The field enhancement factors β of our device is higher compared to the similar device reported in the literature [29]. The higher value β of sample S2 indicates the higher emission current density for a given applied voltage.

The better field emission properties of the device are due to the better quality of the CNTs.

4. Conclusions

In conclusion, we have demonstrated that it is possible to tune the Fe catalyst size and dispersion on MgO support by the addition of small amounts of Mo for the improved synthesis of CNTs. The as-synthesized CNTs using bimetallic catalyst were found to be better for its application as field emitter with respect to the CNTs synthesized with Fe catalyst alone. The synthesis method described in the present study is simple and is potentially scalable.

References

- A. Bianco, K. Kostarelos, C.D. Partidos, M. Prato, Chem. Commun. (2005) 571.
- [2] S.J. Trans, A.R.M. Verschueren, C. Dekker, Nature 393 (1998) 49.
- [3] W.B. Choi, J.U. Chu, K.S. Jeong, E.J. Bae, J.W. Lee, J.J. Kim, J.O. Lee, Appl. Phys. Lett. 79 (2001) 3696.
- [4] Deuk-Seok Chung, et al., Appl. Phys. Lett. 80 (2002) 4045.
- [5] S.J. Tans, M.H. Devoret, H. Dai, A. Thess, R.E. Smalley, L.J. Geerligs, C. Dekker, Nature 386 (1997) 474.
- [6] A. Thess, R. Lee, P. Nikolaev, H.J. Dai, P. Petit, J. Robert, C.H. Xu, Y.H. Lee, S.G. Kim, A.G. Rinzler, D.T. Colbert, G.E. Scuseria, D. Tomanek, J.E. Fisher, R.E. Smalley, Science 273 (1996) 483.
- [7] Z.F. Ren, Z.P. Huang, J.W. Xu, J.H. Wang, P. Bush, M.P. Siegal, P.N. Provencio, Science 282 (1998) 1105.
- [8] M. Joseyacaman, M. Mikiyoshida, L. Rendon, J.G. Santiestebn, Appl. Phys. Lett. 62 (1993) 657.
- [9] L.J. Ci, Y.H. Li, B.Q. Wei, J. Liang, C.L. Xu, D.H. Wu, Carbon 38 (2000) 1933.

- [10] C. Singh, T. Quested, C.B. Boothroyd, P. Thomas, I.A. Kinloch, A.L. Abou-Kandil, A.H. Windle, J. Phys. Chem. B 106 (2002) 10915.
- [11] S. Takenaka, M. Ishida, M. Serizawa, E. Tanabe, K. Otsuka, J. Phys. Chem. B 108 (2004) 11464.
- [12] B.K. Singh, H. Ryu, R.C. Chikate, N.D. Hoa, S.J. Park, S. Kim, J.R. Lee, Solid State Commun. 139 (2006) 102.
- [13] S. Delpeux, K. Szostak, E. Frackowiak, S. Bonnamy, F. Beguin, J. Nanosci. Nanotech. 2 (2002) 481.
- [14] H.J. Jeong, K.K. Kim, S.Y. Jeong, M.H. Park, C.W. Yang, Y.H. Lee, J. Phys. Chem. B 108 (2004) 17695.
- [15] J. Kong, H.T. Soh, A.M. Cassel, C.F. Quate, H. Dai, Nature 395 (1998) 878.
- [16] B. Kitiyanan, W.E. Alvarez, J.H. Harwell, D.E. Resasco, Chem. Phys. Lett. 317 (2000) 497.
- [17] Y. Murakami, Y. Miyauchi, S. Chiashi, S. Maruyama, Chem. Phys. Lett. 377 (2003) 49.
- [18] B.K. Singh, Hojin Ryu, Solid State Phenom. 119 (2007) 227.
- [19] S. Maruyama, R. Kojima, Y. Miyauchi, S. Chiashi, M. Kohno, Chem. Phys. Lett. 360 (2002) 229.
- [20] Y. Murakami, Y. Miyauchi, S. Chiashi, S. Maruyama, Chem. Phys. Lett. 374 (2003) 53.
- [21] A.N. Usoltseva, V.L. Kuznetsov, A.L. Chuvilin, N.A. Rudina, M.Yu. Alekseev, L.V. Lutsev, Carbon 42 (2004) 1037.
- [22] A. Okamoto, H. Shinohara, Carbon 43 (2005) 431.
- [23] K. Takehira, T. Ohi, T. Shishido, T. Kawabata, K. Takaki, Appl. Catal. A: Gen. 283 (2005) 137.
- [24] H.Y. Wang, E. Ruckenstein, Carbon 40 (2002) 1911.
- [25] S. Md, Y.H. Mo, A.K.M. Fazle Kibria, M.J. Kim, K.S. Nahm, Carbon 42 (2004) 2245.
- [26] M.P. Mendoza, C. Valles, W.K. Master, M.T. Martinez, A.M. Benito, Nanotechnology 16 (2005) S224.
- [27] L. Lafi, D. Cossement, R. Chahine, Carbon 43 (2005) 1347.
- [28] Dorota Temple, Materials Science and Engineering R24 (1999) 185.
- [29] Y.M. Wong, S. Wei, W.P. Kang, J.L. Davidson, W. Hofmeister, J.H. Huang, Y. Cui, Diamond Relat. Mater. 13 (2004) 2105.