Available online at www.sciencedirect.com

SCIENCE DIRECT

Diamond & Related Materials 14 (2005) 778–783

DIAMOND AND RELATED MATERIALS

www.elsevier.com/locate/diamond

Structure and property features of the catalyst-assisted carbon nanostructures on Si wafer by catalyst ion implantation and ECR-CVD

Chen Chun Lin, Po Yuan Lo, Chao Hsun Lin, Cheng Tzu Kuo*

Institute of Materials Science and Engineering, National Chiao Tung University, Hsinchu 300, Taiwan

Available online 19 February 2005

Abstract

Experiments to examine effects of ion-implanted catalyst on the structure and property features of carbon nanotubes (CNTs) and nanostructures on Si wafer were conducted by electron cyclotron resonance chemical vapor deposition (ECR-CVD) with CH_4 and H_2 as source gases, under both ion-implanted and PVD-coated catalysts with different H-plasma pretreatment conditions. The deposited CNTs and substrates at every processing step were characterized by FESEM, TEM, SIMS, XRD and Raman spectroscopy. The results show that the growth mechanism of the CNTs under condition with the ion-implanted catalyst is different from that with the PVD-coated catalyst. It results in a greater hollow size of the tubes for the former condition. Furthermore, under conditions of a higher catalyst dosage and higher H-plasma concentration pretreatment, it indicates better field emission properties, more Co-silicide formation and more percentage of base-growth CNTs due to an increase in the amount of Co source and process temperature. The main effect of the implanted catalyst is essentially to enhance the adhesion strength of CNTs with the substrate through the Co-silicide formation and embedding the catalyst into the substrate, as shown by XRD and SIMS analyses. Additionally, it is also favor to form CNTs with a lower I_D/I_G ratio and so a lower defect density. Under the present conditions, the best field emission properties are: turn-on voltage ~6 V/μm and current density>0.72 mA/cm^2. In summary, the structure, growth mode, adhesion strength with the substrate, defect density and field emission properties of CNTs can be manipulated by changing the ion-implantation dosages and H-plasma pretreatment conditions, which may not be able to be produced by other methods.

Keywords: Carbon nanotubes (CNTs); Catalysts; Ion implantation; Plasma CVD; Field emission

1. Introduction

Since the discovery of carbon nanotubes (CNTs) by Iijima [1], the CNTs have attracted great interest in nanotechnology due to their special characters and properties. This novel material can have many potential applications, such as scanning probe [2], supercapacitors [3], hydrogen storage [4,5] and field emission displays due to their nano-scale sizes at both the tip and diameter of the tubes [6,7]. Many methods for growing CNTs have been proposed, including arc discharge [8], laser vaporization [9], microwave plasma CVD (MPCVD) [10], hot filament-CVD (HF-CVD) [11], ECR-CVD [12], thermal CVD [13], etc. Although the ECR-CVD method takes the advantages of growing the well-aligned CNTs on a larger area [12], all these methods are generally giving a serious drawback of poor adhesion on the substrate.

Ion implantation is a useful technology in bipolar junction transistors to control their electric properties. In order to increase adhesion of CNTs on the substrate, we try to take the advantages of ion implantation to penetrate the catalyst into the substrate to enhance the interaction of catalyst with the substrate. Recently, one way to enhance the adhesion of CNTs on the substrate was proposed by high temperature annealing of the PVD-coated catalyst

* Corresponding author. Tel.: +886 3 5731949; fax: +886 3 5721065.
E-mail address: ctkuo@mail.nctu.edu.tw (C.T. Kuo).

0925-9635/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.diamond.2004.12.031

before CNTs deposition [14]. However, such a high temperature process is not suitable for integration with IC process. In this paper, we combine the ECR-CVD process with the catalyst ion-implantation process to examine their effects on properties of the deposited CNTs.

2. Experimental

The Co-catalyst-assisted CNTs were synthesized on Si wafers by using ECR-CVD with CH_4 and H_2 as source gases. In order to examine the effect of catalyst ion implantation, the Co-catalysts were deposited on Si wafer by either PVD method or ion implantation. The substrates were subjected to three different ion-implantation dosages. The ion implantation was carried out in an implanter by varying the implantation time under 10^{-5} Torr pressure, 30 μA trigger current and 60 kV voltage. The implanted or coated substrates were then pretreated in hydrogen plasma to become the well-distributed nano-particles before CNTs deposition. The plasma pretreatment processes were conducted at two different conditions (con1 and con2), which are used to divide the specimens into two groups ("xxxa" and "xxxb"). The detailed catalyst pretreatments and CNT deposition conditions together with specimen designations are shown in Table 1.

The film morphologies, nanostructures, interface profile and crystal structures at various processing steps were characterized by FESEM, TEM, SIMS and XRD. The bonding structures were examined by Raman spectroscopy. The field emission properties were measured using an I-V detector with anode–cathode distance of 104 μm under 10^{-5} Torr.

3. Results and discussion

3.1. Effect of ion implantation on CNTs growth mechanism

Fig. 1(a) and (b) show TEM micrographs of CNTs with the implanted and PVD-coated catalysts, respectively. It indicates that the hollow size (~6 nm) of the CNTs with the implanted catalysts are generally greater than that (~4 nm) with the PVD-coated catalysts. In other words, carbon atoms from the gas phases are more favor to precipitate on the outer shells of the CNTs with greater hollow sizes. This can be explained as follows. At beginning of the CNT growth, the diffusion paths of carbon atoms to form CNTs from the embedded or implanted catalysts are believed more favor to precipitate carbon on the outer shells of each tube, which are the cooler locations at the catalysts/substrate interfaces by conducting the heat through the substrate. After each CNT nucleation, the carbon atoms prefer to precipitate on the outer shells of each CNT due to smaller diffusion paths and blocking effect of the existing carbon shells. In contrast, for the PVD-coated catalysts without being embedded by the substrate, the diffusion paths of carbon atoms will have more equal opportunities to precipitate along the lower catalyst surface to form more shells at beginning of the CNT growth to cause a smaller hollow size. This implies that the implanted catalysts are more favor to grow tubule-like CNTs with greater hollow sizes by changing the local heat flow patterns.

Fig. 2(a)–(c) are SEM micrographs of CNTs under the same H-plasma pretreatment condition (con1) but with three different catalyst ion-implantation dosages (0.32×10^{16}, 1.56×10^{16} and 5.20×10^{16} cm^{-2}), respectively. It is interesting to note that there is an optimum dosage to give the

Table 1
Specimen designations for CNTs deposited[a] by using different catalysts and H-plasma pretreatment conditions (a) for ion-implanted catalysts, and (b) for PVD-coated catalysts

(a)

Specimen designation	Catalyst material	Implantation dosage (10^{16} cm^{-2})	Plasma pretreatment condition[b]	Growth mechanism	Tube number density (tubes/μm^2)
IM1a	Co	0.32	con1	tip	3.5
IM1b			con2	tip+base	low
IM2a		1.56	con1	tip	8.5
IM2b			con2	tip+base	middle
IM3a		5.20	con1	tip	1.8
IM3b			con2	base	10.5

(b)

Specimen designation	Catalyst material	Film thickness (nm)	Plasma pretreatment condition[b]	Growth mechanism
SP1a	Co	20	con1	tip
SP1b			con2	tip

[a] Deposition conditions of CNTs: 800 W microwave power, 10^{-3} Torr, CH_4/H_2=10/10 sccm/sccm, 15 min, −200 V bias, ~530 °C average temperature.
[b] Hydrogen plasma etching conditions for specimens of "a" and "b" series: (1) con1: for "a" series, 800 W microwave power, 10^{-3} Torr, 15 min, −200 V bias, ~485 °C average temperature, 10 sccm H_2; (2) con2: for "b" series, same as con1, except ~540 °C average temperature, 15 sccm H_2.

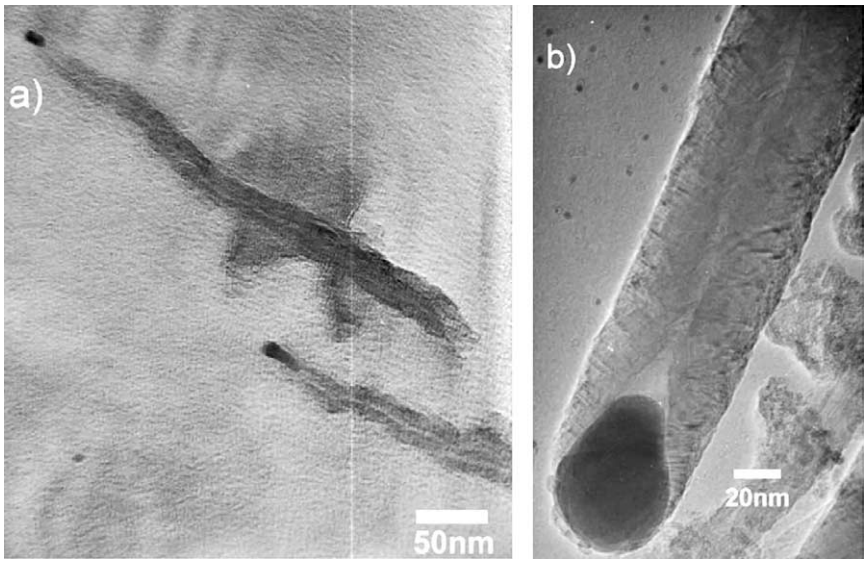

Fig. 1. TEM micrographs of the CNTs under (a) the implanted-catalyst, and (b) the PVD-coated catalysts.

maximum tube number density, as shown also in Table 1. It also shows that the CNTs are tip-growth multi-walled CNTs independent of ion dosage levels. In contrast, under the higher H-plasma concentration pretreatment condition (con2), the CNTs or carbon nanostructures are gradually changed from mixing mode of tip- and base-growth to complete base-growth mode by increasing the ion dosage level, as shown in Table 1 and Fig. 2(d), where Fig. 2(d) shows the SEM micrograph of carbon nanostructures under a higher H-plasma concentration pretreatment condition (con2) and the highest implantation dosage level (5.20×10^{16} cm^{-2}). It indicates that carbon nanostructures are much shorter in length, bigger in diameter and with no catalysts at the tips, signifying the base-growth nanostructures. The shorter and bigger carbon nanostructures in this case may be due to the following reasons. A higher dosage level can result in a greater particle size and the embedded depth of the catalysts. In other words, a greater

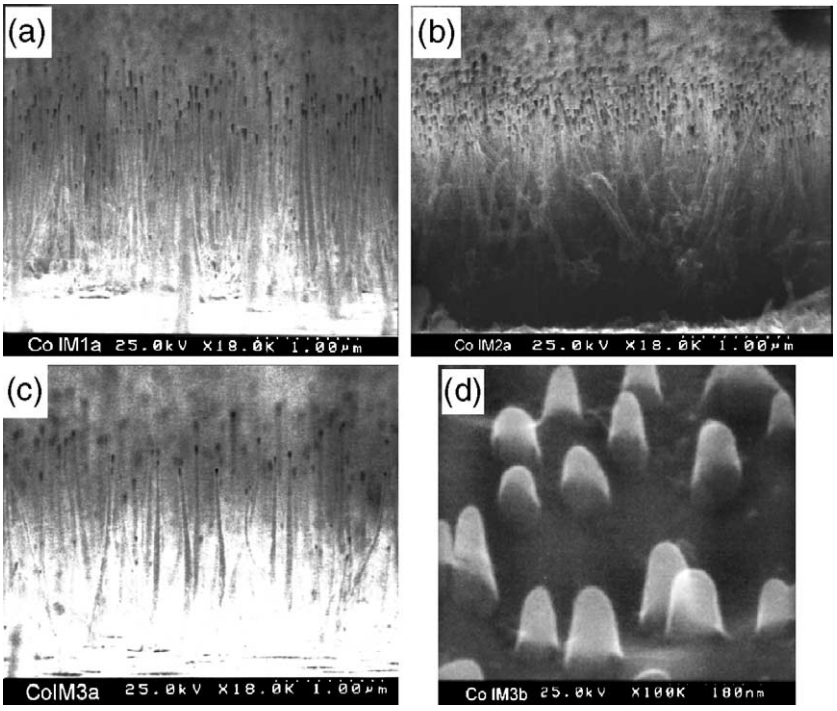

Fig. 2. SEM micrographs of the typical implanted-Co-assisted CNTs under the lower H-plasma concentration conditions and (a) 0.32×10^{16}, (b) 1.56×10^{16} and (c) 5.20×10^{16} cm^{-2} ion-implantation dosages, and (d) under a higher H-plasma concentration pretreatment condition with 5.20×10^{16} cm^{-2} ion-implantation dosages.

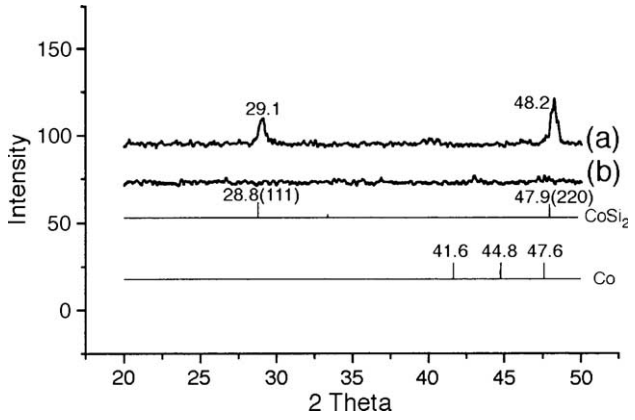

Fig. 3. XRD patterns of the as-implanted substrates by Co with different dosage levels (a) 1.56×10^{16} and (b) 0.32×10^{16} cm^{-2} dosages.

particle size is expected to grow a bigger but shorter carbon nanostructure; furthermore, a greater embedded depth can give rise to a greater tendency to be poisoned to become shorter nanostructures due to a greater restriction in surface area for carbon precipitation through the catalyst. The growth mode of nanostructures or CNTs may be related to the amount of $CoSi_2$ formation. Under higher H-plasma concentration condition (con2) and higher ion dosage level, it results in a greater pretreatment temperature, more Co-silicides formation, and so a lower melting temperature (m.p. of Co>Co-silicides) [15]. In other words, a higher H-plasma concentration can give rise to more Co-silicides formation, stronger bonding with the substrate and so more base-growth carbon nanostructures formation, especially at higher ion dosage level, as shown in Fig. 2(d). To examine the possible reaction of catalyst with the substrate, the XRD patterns of the as-implanted substrates at two different dosages of 1.56×10^{16} and 0.32×10^{16} cm^{-2} are shown in Fig. 3(a) and (b), respectively. It indicates that a higher dosage level gives rise to greater intensity of $CoSi_2$ peaks due to a higher temperature at higher dosage. Formation of the Co-related compounds for the contact and gate materials, e.g., $CoSi_2$, is widely known in sub-micron IC technologies [16,17]. The greater tendency of Co-silicides formation under higher ion dosage level or higher H-plasma concentration is in agreement with the results of the CNTs growth mode analyses.

3.2. Effect of ion implantation on adhesion of CNTs on the substrate

The CNTs synthesized under the implanted and PVD-coated catalysts were scratched by a diamond pencil or agitated in an ultrasonic acetone bath for 10 min to examine the amount of remaining CNTs on the surface. Under the implanted catalyst condition, the results show that some branches of CNTs were scratched off by the diamond pencil from the substrate, but their roots were remained in the substrate (Fig. 4(a)). Furthermore, the tips of CNTs were found to stick together, and the CNTs were remained standing on the substrate by agitating in the acetone bath (Fig. 4(b)). In contrast, for the CNTs under the PVD-coated catalyst condition, there are no CNTs left on the substrate after scratching or agitating in bath. In other words, the CNTs under the implanted catalyst condition are essentially embedded below the substrate surface, and clipped by the surrounding Si walls. This is in agreement with the results of secondary ion mass spectroscopy (SIMS) that some of the catalysts and carbons are embedded in the substrate to enhance the adhesion of the implanted-catalyst-assisted CNTs.

3.3. Effect of ion implantation on bonding and defect features

Fig. 5(a) and (b) show Raman spectra of CNTs under the PVD-coated and the implanted catalysts, respectively.

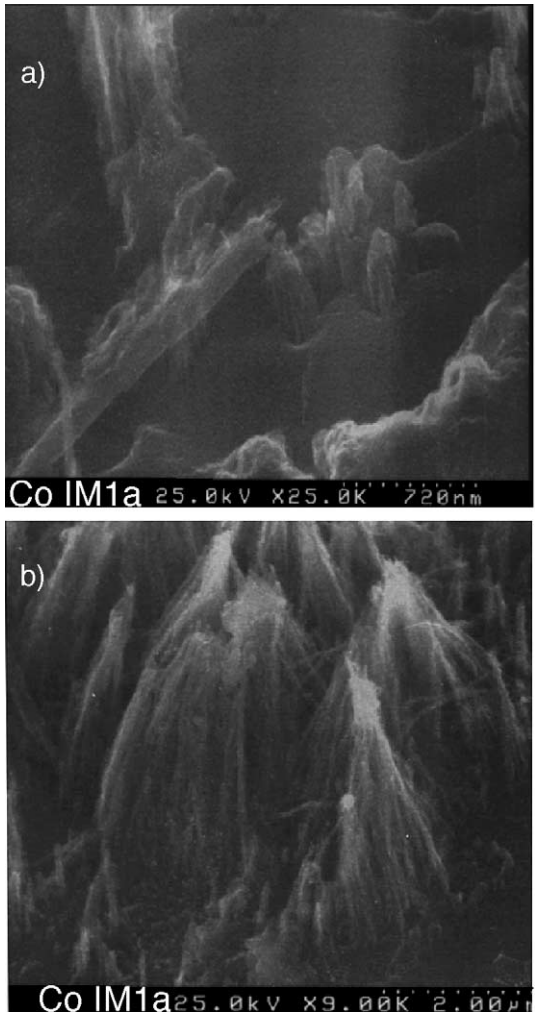

Fig. 4. SEM micrographs of the fracture surface of CNTs on Si wafer under the Co-implanted catalyst and lower H-plasma pretreatment conditions by (a) scratching with a diamond pencil, and (b) agitating in ultrasonic acetone bath for 10 min.

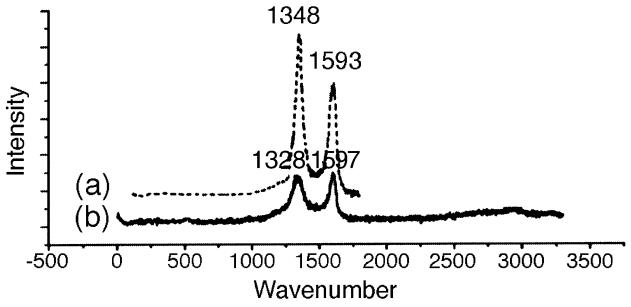

Fig. 5. Raman spectra of the catalyst-assisted CNTs under (a) PVD-coated and (b) ion-implanted catalyst conditions.

Their intensity ratios of D-band and G-band (I_D/I_G) are about 1.4 and 1.3, respectively, where the value of 1.3 is for CNTs under lower H-plasma concentration and lower ion dosage level conditions. The results also indicate that values of I_D/I_G ratios for CNTs under the implanted catalyst condition are ranging from 0.9 to 1.3, and are a function of H-plasma concentration and ion dosage level. A higher H-plasma concentration and higher dosage level are more favor to give a lower ratio, and so a lower defect density. In other words, the defect density for CNTs under the implanted catalyst condition is generally less than that under the PVD-coated catalyst condition. This can be proved by SEM examination at cross section of CNTs that the implanted-catalyst-assisted CNTs possess less a-C film at the substrate interface. A lower defect density may relate to smaller tube diameter and greater hollow size of the tube, or may relate to more silicide formation to decrease the melting temperature of the catalyst. Further study is necessary.

3.4. Effect of ion implantation on field emission properties

The J–E curves and the corresponding F–N curves for the implanted-Co-assisted CNTs are shown in Fig. 6. It indicates that the CNTs with more tip-growth mode generally give rise to poorer field emission properties than that with more base-growth mode. This may relate to the blocking effect of the catalysts at the tips of the CNTs and a less tube number density. In other words, the CNTs under a higher H-plasma concentration pretreatment and higher dosage level will possess better field emission properties. It is interesting to note that a higher tube number density results in better field emission properties. This is reasonable from the point of higher geometrical enhancement factor for a higher tube number density due to a smaller diameter of the tubes and so a higher aspect ratio, if the tube number density is not too high to screen each other from the neighbor CNTs, as also shown in Table 1. It is also found that the overall field emission properties of the ion-implanted CNTs are quite high by comparing with that of the PVD-coated-Co-assisted nanotubes prepared in this laboratory [18]. It seems to be related to a smaller tube number density under the present conditions. Under the present conditions, the best field emission properties are: turn-on voltage=6 V/μm at 1 μA/cm^2 current density, current density>0.72 mA/cm^2 at 10 V/μm. Further improvement is possible.

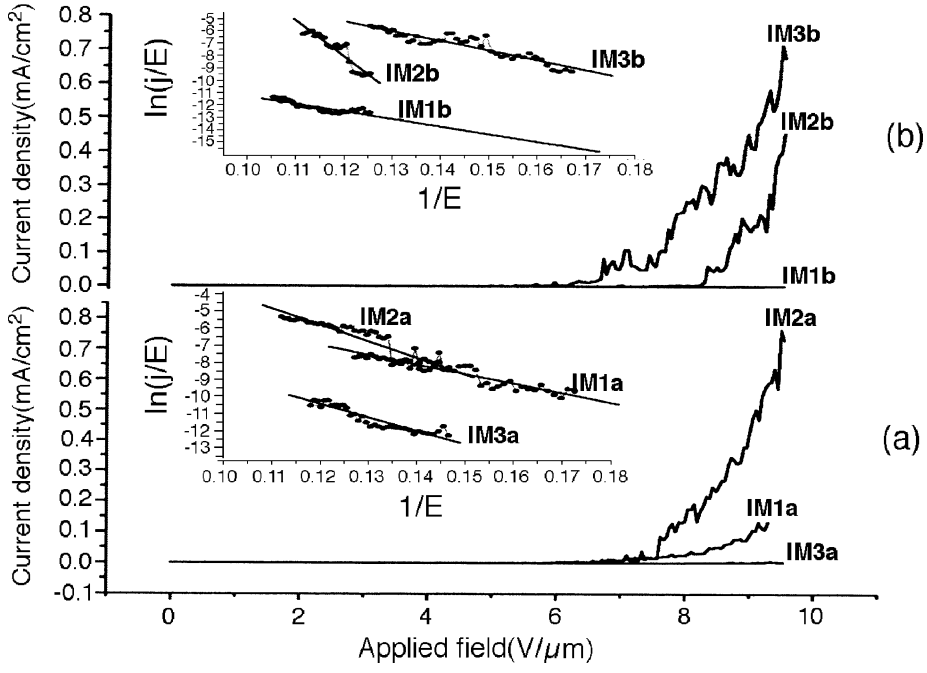

Fig. 6. J–E curves and the corresponding F–N plots for the implanted-catalyst-assisted CNTs under different ion dosage levels and H-plasma pretreatment conditions (a) lower H-plasma and (b) higher H-plasma concentrations.

4. Conclusions

Using Co as the catalyst, the different nanostructures and properties of carbon have been successfully synthesized by ECR-CVD method through manipulating the ion implantation and H-plasma pretreatments to vary the catalyst size, quantity and embeddings in the substrate. The results show that ion implantation is essentially to embed the catalyst into the substrate, to enhance the interaction of catalyst with the substrate and to guide the initial precipitation-growth stage of CNTs. Therefore, in the present conditions, ion implantation favors the following effects: (1) decreasing the a-C film formation, (2) increasing the hollow sizes of CNTs, (3) increasing the adhesion of CNTs on the substrate, (4) decreasing the Raman I_D/I_G ratio, i.e. forming less defect CNTs, (5) enhancing base-growth mode, and (6) changing the tube number density of CNTs. For the implanted Co-catalysts at greater dosages, it is essentially to grow CNTs by using $CoSi_2$ as catalyst and to enhance the adhesion with the substrate. The best field emission properties (turn-on voltage ~6 V/μm, current density>0.72 mA/cm^2) are CNTs under higher H-plasma concentration pretreatment condition and higher ion dosage level of 5.2×10^{16} cm^{-2}. In summary, the H-plasma pretreatment and ion-implanted catalysts can be used to manipulate the growth of nanostructures to obtain many special features, which may not be able to be produced by other methods.

References

[1] S. Iijima, Nature 354 (1991) 56.
[2] H. Dai, J.H. Hafner, A.G. Rinzler, D.T. Rinzler, D.T. Colbert, R.E. Smalley, Nature 384 (1996) 147.
[3] G. Che, B.B. Lakshmi, E.R. Fisher, C.R. Martin, Nature 393 (1998) 346.
[4] C. Journet, W.K. Maser, P. Bernier, A. Loiseau, M. Lamy de la Chapelle, S. Lefrant, P. Deniered, R. Lee, J.E. Ficher, Nature 308 (1997) 756.
[5] A.C. Dillon, K.M. Jones, T.A. Bekkedahl, C.H. Kiang, D.S. Bethune, M.J. Heben, Nature 386 (1997) 377.
[6] F. Ito, K. Konuma, A. Okamoto, J. Appl. Phys. 89 (2001) 8141.
[7] Q.H. Wang, A.A. Setlur, J.M. Lauerhaas, J.Y. Dai, E.W. Seelig, R.P.H. Chang, Appl. Phys. Lett. 72 (1998) 22.
[8] D.S. Bethune, C.H. Klang, M.S. de Vries, G. Gorman, R. Savoy, J. Vazquez, R. Beyers, Nature 363 (1993) 605.
[9] A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y.H. Lee, S.G. Kim, A.G. Rinzler, D.T. Colbert, G. Scuseria, D. Tomanek, J.E. Fisher, R.E. Smalley, Science 273 (1996) 483.
[10] L.C. Qin, D. Zhou, A.R. Krauss, D.M. Gruen, Appl. Phys. Lett. 72 (1998) 3437.
[11] Z.F. Ren, Z.P. Huang, J.W. Xu, J.H. Wang, P. Bush, M.P. Siegal, P.N. Provencio, Science 282 (1998) 1105.
[12] S.H. Tasi, F.K. Chiang, T.G. Tsai, F.S. Shieu, H.C. Shih, Thin Solid Films 366 (2000) 11.
[13] S. Fan, M.G. Chapline, N.R. Franklin, T.W. Tombler, A.M. Cassel, H. Dai, Science 283 (1999) 512.
[14] C. Bower, Otto Zhou, Wei Zhou, D.F. Wender, Sungho Jin, Appl. Phys. Lett. 77 (17) (2000) 2767.
[15] R.T. Tung, Appl. Phys. Lett. 68 (1996) 3461.
[16] K. Maex, M.V. Rossum, In properties of metal silicides, INSPEC, 1995.
[17] K.K. Ng, W.T. Lynch, IEEE Trans. Electron Devices ED 34 (1987) 503.
[18] Chih-Ming Hsu, Sheng-Chin Kung, Bean-Jon Li, Hong-Jen Lai, Cheng-Tsou Kou, J. Vac. Sci. Technol., A, Vac. Surf. Films 22 (4) (2004) 1461.