ELSEVIER

Diamond and Related Materials 11 (2002) 1638–1642

DIAMOND AND RELATED MATERIALS

www.elsevier.com/locate/diamond

Fabrication of vertically aligned carbon nanotubes patterns by chemical vapor deposition for field emitters

W.D. Zhang[a,*], J.T.L. Thong[b], W.C. Tjiu[a], L.M. Gan[a]

[a]*Institute of Materials Research and Engineering, 3 Research Link, Singapore 117602, Singapore*
[b]*Centre for Integrated Circuit Failure Analysis and Reliability (CICFAR), Faculty of Engineering, National University of Singapore, 4 Engineering Drive 3, Singapore 117576, Singapore*

Received 26 November 2001; received in revised form 3 April 2002; accepted 11 April 2002

Abstract

A simple and reliable method has been developed for the controlled growth of well-aligned carbon nanotubes patterns with different sizes and shapes on a silicon substrate. A patterned film of sputtered cobalt on the silicon was prepared by a lift-off process, and the carbon nanotubes were grown via chemical vapor deposition using ethylenediamine as a precursor. The carbon nanotubes are vertically aligned with high density within the micro patterns. The diameter of carbon nanotubes is determined by the thickness of cobalt film while the length of the nanotubes can be controlled by varying the reaction time. The bamboo-like multi-walled carbon nanotubes have been observed by high-resolution transmission electron microscopy. The micro-Raman spectrum further confirmed the graphitic structure of the nanotubes. The potential application of the carbon nanotubes to flat-panel displays is demonstrated by the ability to provide stable high field-emission current densities.

Keywords: Carbon nanotubes; Patterns; Field emission; Chemical vapor deposition

1. Introduction

The discovery of carbon nanotubes (CNTs) [1] has attracted much attention with potential applications in nanoelectronics and nanomanipulation based on their remarkable physical properties [2–5]. It is also a promising candidate as a cold field emitter for flat panel displays due to their small tip radii of curvature, high mechanical strength and high chemical stability [6]. Full color displays have been fabricated based on CNT electron sources, which were prepared by an arc-discharge method and aligned on glass plates by pasting [7]. In order to simplify the process, it is desirable to grow CNTs directly on the cathode plate with good alignment. Well-aligned CNTs arrays have been grown on quartz plates by pyrolysis of organometallic precursors [8–10] or hydrocarbon–ferrocene (ferric carbonyl) mixture [11–13]. Other methods for direct growth of well-aligned CNTs are more compatible with current silicon fabrication techniques for electronic applications. Kind et al. realized well-aligned growth of CNTs on silicon wafers using microcontact printing of catalysts [14]. Li et al. grew CNTs on porous silicon pre-etched with HF [15] while Ren et al. used NH_3-etched substrate and a plasma-enhanced CVD process [16,17]. More recently, Lee et al. synthesized aligned CNTs on metal-deposited silicon wafers pre-etched with HF and NH_3 [18–20]. However, it is still a challenge to directly fabricate CNTs field emitter for commercial applications. In this letter, we introduce a simple and reliable method for patterned growth of vertically aligned CNTs on silicon dies by chemical vapor deposition with ethylenediamine as a precursor. Field emission from a 3.6×10^{-3} cm^2 patterned array has also been examined.

2. Experimental

Patterns of approximately 5–20-nm thick cobalt with different sizes and shapes were fabricated by conventional optical lithography on a p-type silicon substrate of 3–10 Ω cm^{-1} resistivity by sputtering and lift-off. In order to get better electronic conductivity, we also fabricated patterned cobalt films on gold-coated silicon

*Corresponding author. Tel.: +65-6874-1993; fax: +65-6872-0785.

E-mail address: wd-zhang@imre.org.sg (W.D. Zhang).

0925-9635/02/$ - see front matter
PII: S0925-9635(02)00110-3

dies. Carbon nanotubes were synthesized on the patterned Co film using chemical vapor deposition at 800–900 °C with ethylenediamine as a precursor. After reaction for 5–30 min, the reactor was cooled down to room temperature in N_2 ambient. A scanning electron microscope (SEM) (Philips XL 30 FEG) was used to observe the surface morphology, the length and the alignment of the synthesized CNTs. The quality and layer structure of CNTs was examined using a transmission electron microscope (TEM) (Philips CM 300 FEG). A confocal microscope Raman spectroscope (Dilor LabRam I) was used to confirm the graphitized structure of CNTs with a 632.8-nm He–Ne laser. A planar diode configuration was adopted for the field-emission measurements. The silicon die with the CNT array was attached to the cathode plate, while a similar silicon die attached to the anode plate presents a smooth anode surface. The spacing between the anode and the top of the CNT array is 935 ± 10 μm. The assembly was placed in a UHV chamber, baked out and evacuated for over 24 h. Measurements were carried out at vacuum levels of better than 10^{-8} mbar.

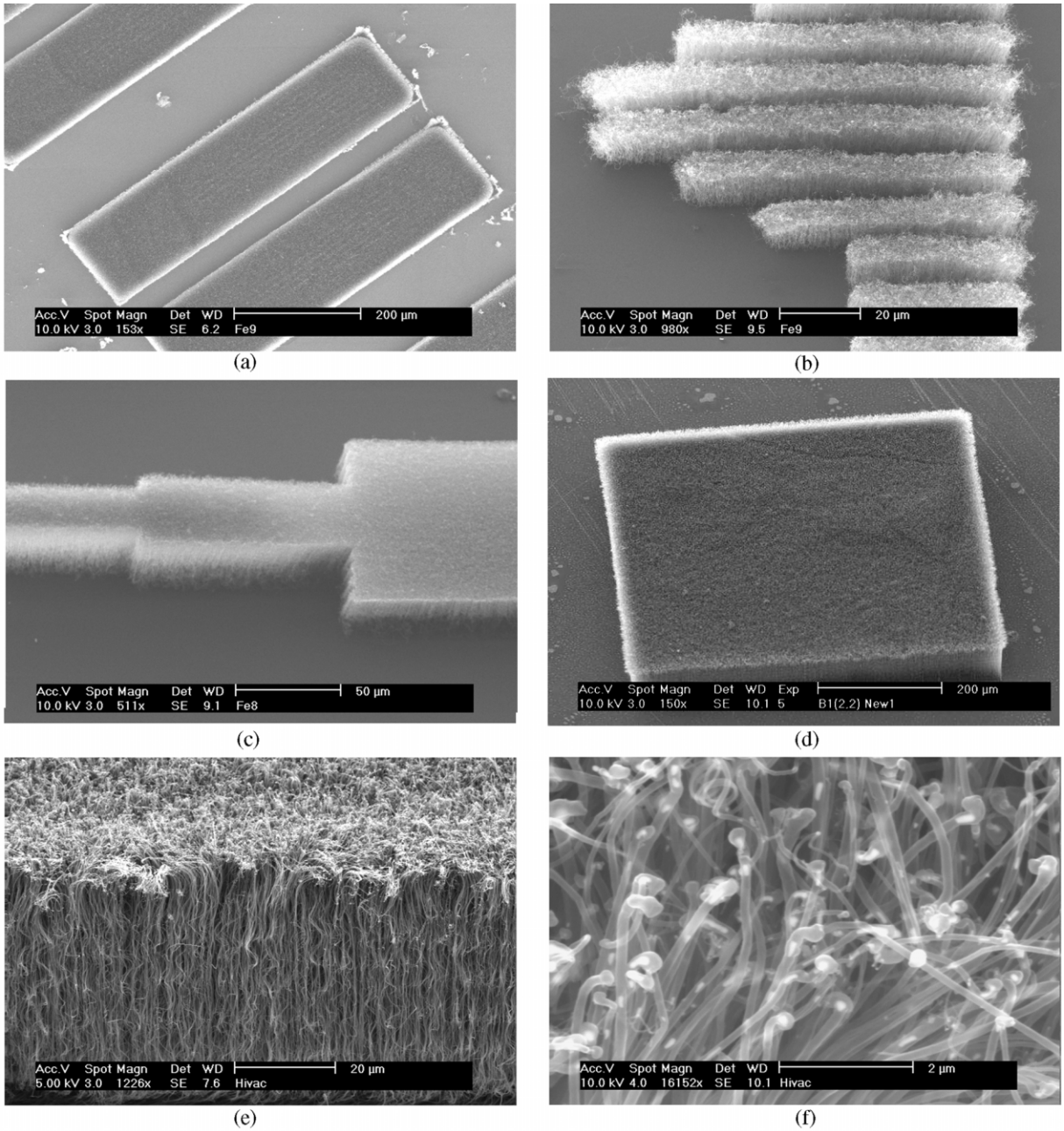


Fig. 1. SEM images of aligned carbon nanotubes patterns: (a) top view of rectangle patterns; (b–d) samples were tilted at 25°; (e) zoom in side view of the aligned CNTs; (f) zoom in top view of CNTs, showing bright dots embedded in the top ends and along the tubes.

3. Results and discussion

After CVD, black CNT films were formed within the area defined by the patterned cobalt on the silicon die. Fig. 1a–d shows SEM images of carbon nanotubes patterns with different shapes and sizes synthesized on the surface of silicon die by CVD of ethylenediamine. The patterns of CNTs were strictly confined to the patterned areas and have definite morphology. No carbon nanotubes were formed on the surface where cobalt was not present. All of the nanotubes are almost the same height. The densely packed CNTs are perpendicularly aligned on the surface of silicon die. In order to increase the electronic conductivity, we also grew vertically aligned CNTs on gold-coated silicon dies with cobalt patterns. Fig. 1d shows a low-magnification SEM image of a 3.6×10^{-3} cm^2 square CNT array grown on a 20-nm cobalt film for 30 min. The CNTs are perpendicularly aligned with high density in the region of the surface with cobalt. Outside the Co pattern, one can see some metal dots. Energy dispersive X-ray analysis (EDX) confirmed that the metal dots are gold which resulted from the sintering of the thin gold film at high temperature. The zoom-in view of the CNTs shown in Fig. 1e,f indicate that most of the tubes are approximately 150 nm in diameter but some much smaller tubes are also present in the nanotube bundles. Furthermore, one can also see that some bright dots enclosed in the tips and some even distributed along the length of the tubes. EDX shows that these bright dots are cobalt particles. However, EDX spectra taken from the roots of the peeled off aligned CNTs shows that the roots contain only carbon. This indicates that the aligned CNTs resulted from tip growth, i.e. the seeded cobalt particles were lifted up as the CNTs grew.

The length of the CNTs can be easily controlled by varying the CVD reaction time. The growth rate of CNTs is fast at the outset and then slows down as the CVD reaction time increases since the seeded Co particles would have been encapsulated by graphite layers. During the initial 5 min, the average growth rate of CNTs is approximately 3 μm min^{-1}, which produced 15 μm CNTs. The CNTs were approximately 50 μm at a run of 30 min. The effect of thickness of the Co film on the diameter of tubes has also been studied. The results show that when the thickness of the Co film increases from approximately 5 to 40 nm, the diameter of the nanotubes increases from approximately 80 to 150 nm. Furthermore, thicker cobalt films produce higher density CNTs and thus the three-dimensional CNTs patterns have very well-defined edges and corners (Fig. 1c,d).

The growth mechanism of CNTs by catalytic CVD of hydrocarbons has been explained as the decomposition of the precursor by metal catalysts such as Fe, Co, Ni, etc [15]. In our method with ethylenediamine as precursor for the growth of CNTs on silicon dies, ethylenediamine not only provides the carbon, but it is also essential for the vertical alignment of CNTs. The cobalt thin film was sintered at elevated temperature in the initial stages of the CVD. The amine promoted the formation of cobalt nanoparticles from the film which then served as seeds for CNT growth. Fig. 2 shows the cobalt-coated silicon die after CVD of ethylenediamine for 2 min. One can see that high density of cobalt nanoparticles were formed. The high density of cobalt particles gave rise to the CNT arrays of high density. Van de Waals forces between the tubes hold the nanotubes together, thus enabling vertical growth on the surface of silicon dies. Thicker cobalt films ranging from 5 to 50 nm result in bigger cobalt particles with higher density during CVD, leading to thicker CNTs of higher density, whereas thinner cobalt films result in smaller cobalt particles that are more sparsely distributed thereby producing thinner CNTs with lower density. Cobalt films thinner than 5 nm result in a sparse distribution of cobalt particles, and thus the CNTs formed are sparse. However, very thick cobalt films fail to separate into nanoparticles for CNT growth via CVD. We found that the CNTs grown on the silicon dies without gold coating are more uniform in diameter. In the case with gold coating, the cobalt and gold sinters together and forms an alloy at high temperature. However, the Co particles are still able to serve as seeds for the CNTs growth. We also noticed that sputtered cobalt on the silicon surface can diffuse into the silicon crystal after several days and CNT cannot grow with these samples. On a gold-coated silicon die, the diffusion of cobalt was inhibited and CNT can grow on such dies even after the cobalt has been sputtered for several weeks.

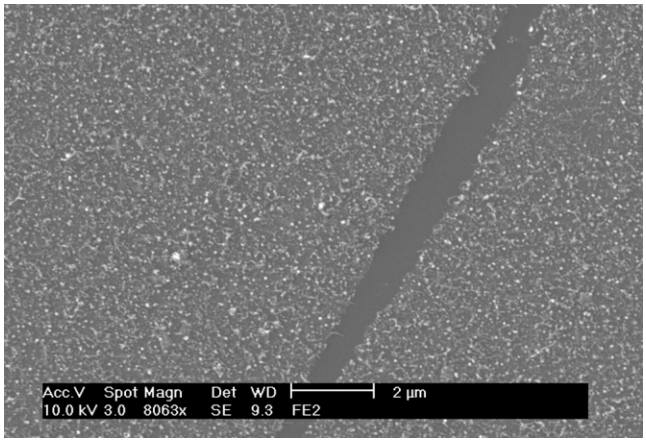
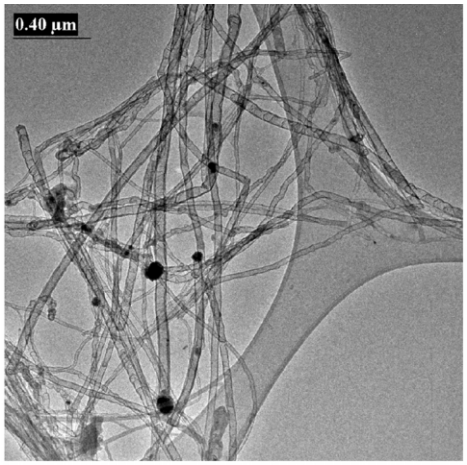
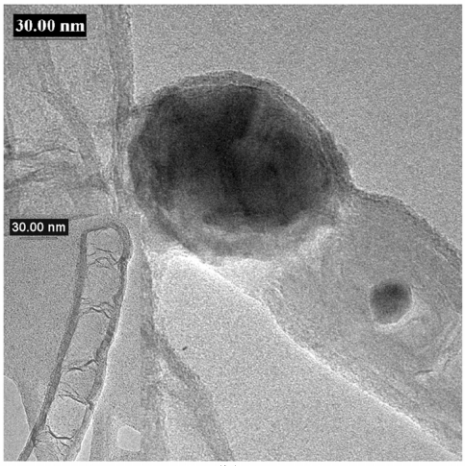


Fig. 2. SEM image of Co particles which formed from 20-nm thick Co film after CVD of ethylenediamine for 2 min.

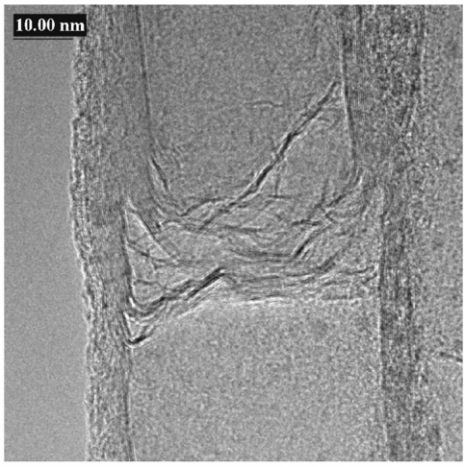
Fig. 3a shows a low magnification TEM image of the CNTs. Most of the carbon nanotubes are closed at both



(a)



(b)



(c)

Fig. 3. (a) Low magnification TEM image of CNTs, (b) a CNT tip embedded with a metal particle in the end and another smaller one adjacent to the end, inset shows another closed end of a CNT without Co particle, (c) high resolution TEM image of a CNT with graphite wall layers and loosely graphite block layers.

ends—each nanotube contains a Co particle at one end. Some of the cobalt particles are at the ends of much larger closed and bulbous tips. Fig. 3b shows a tube with a cobalt particle in the end while another smaller one is embedded in the tube adjacent to it. The inset shows another closed end of the tube. The tubes have a bamboo-like structure, i.e. the hollow of the tube is separated by loose graphitic layers at an interval of approximately 20–50 nm. The TEM result is coincident with the result of SEM, i.e. the tubes are the result of tip growth and the metal particles were lifted-up as the tubes grew. Some of the cobalt particles were also embedded along the tubes. This phenomenon has previously been observed and it has been postulated that the metal nanoparticles were in liquid state during nanotube growth [21]. The high-resolution TEM image shows that the graphite layered sidewalls of the CNT are aligned with a tilted angle of approximately 10° toward the tube axis (Fig. 3c). The tube contains approximately 20–50 graphite wall layers and approximately 10–20 blockage layers.

The graphite structure of the prepared CNTs is clearly demonstrated by the micro-Raman spectrum (Fig. 4) with a strong band at 1593 cm^{-1}, which corresponds to the G-line of multi-walled CNTs [22]. The D-line peak at 1313 cm^{-1} has been known to be attributed to the defects in the curved graphene sheet, tube ends and finite size of crystalline domains of the tubes [23,24]. Therefore, the Raman spectrum provides definite evidence that the CNTs have multi-walls with graphitic structure.

The electron field emission characteristics of a 3.6×10^{-3} cm^2 patterned array of CNTs is shown in Fig. 5. An I–V measurement was first carried out on the CNT array using a planar diode configuration with an anode to cathode spacing of 0.935 mm. The maxi-

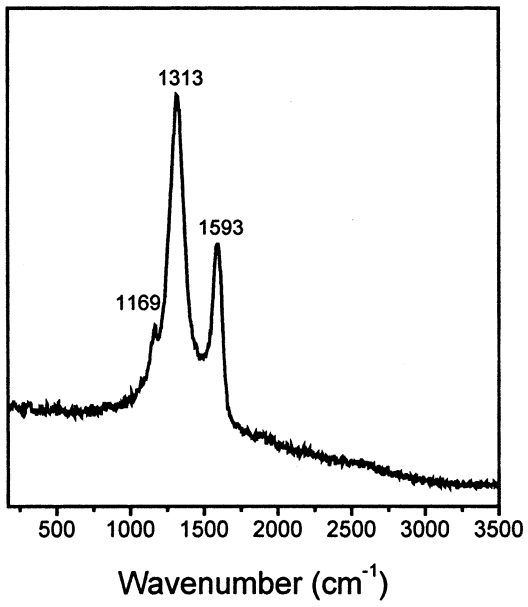


Fig. 4. Raman spectrum of the as-prepared CNTs.

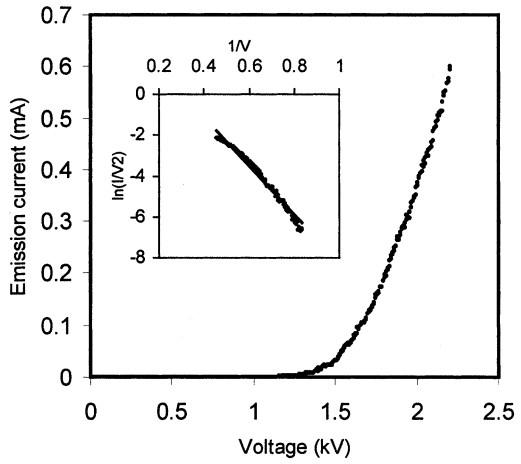


Fig. 5. Field-emission I–V characteristics. Anode-to-cathode spacing is 0.935 mm. Inset shows the corresponding Fowler–Nordheim plot.

mum applied voltage of 2.2 kV corresponds to an average 'planar' field of 2.35 V μm^{-1}. At 2.2 kV, the emission current is 0.6 mA, corresponding to a current density of 166 mA cm^{-2} averaged over the area of the array. For comparison with other reported works, the threshold field to produce 10 mA cm^{-2} is 1.6 V μm^{-1}. The emission current at constant voltage also shows good short-term stability (Fig. 6), with fluctuations of approximately $\pm 2\%$ (5 Hz measurement bandwidth) when the measurement was performed at a vacuum of better than 10^{-8} mbar.

4. Conclusion

In summary, vertically aligned CNTs have been selectively grown on deposited cobalt patterns on silicon dies by CVD without plasma assistance. The well-aligned CNTs patterns are strictly confined within the perimeters of the cobalt-film patterns in micro scale. The density and diameter of CNTs were determined by the thickness of Co-film, while the length of CNTs was controlled by the CVD reaction time. The CNTs have bamboo-like multi-walled structure and are closed at both ends with a cobalt particle at each top end. The method outlined here for the synthesis of patterned well-aligned carbon nanotubes on silicon dies is compatible with current silicon device processing techniques for the fabrication of practical nanotubes electronic devices. With a 3.6×10^{-3} cm^2 CNT array, high emission current at low voltage has been achieved.

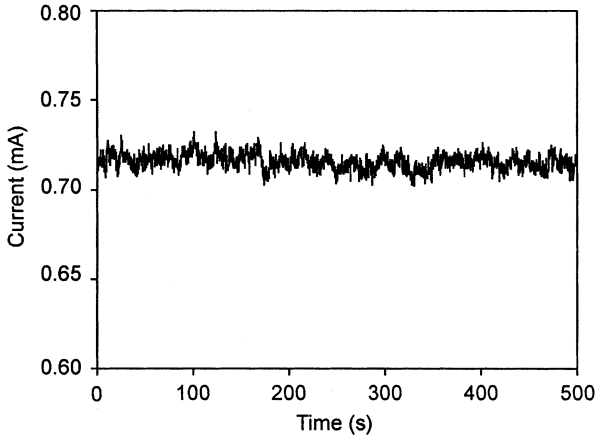


Fig. 6. Short-term stability measurement. Measurement bandwidth = 5 Hz.

References

[1] S. Iijima, Nature (London) 354 (1991) 56.
[2] W.A. de Heer, A. Chatelain, D. Ugarte, Science 270 (1995) 1179.
[3] P.G. Collins, A. Zettl, H. Bando, A. Thess, R.E. Smalley, Science 278 (1997) 100.
[4] P. Kim, C.M. Lieber, Science 286 (1999) 2148.
[5] S.S. Wong, E. Joselevich, A.T. Woolley, C.L. Cheung, C.M. Lieber, Nature 394 (1998) 52.
[6] Q.H. Wang, A.A. Setlur, J.M. Lauerhaas, J.Y. Dai, E.W. Seelig, R.P.H. Chang, Appl. Phys. Lett. 72 (1998) 2912.
[7] W.B. Choi, D.S. Chung, J.H. Kang, et al., Appl. Phys. Lett. 75 (1999) 3129.
[8] C.N.R. Rao, R. Sen, B.C. Satiskhumar, A. Govindaraj, Chem. Comm. (1998) 1525.
[9] B.C. Satishkumar, A. Govindaraj, C.N.R. Rao, Chem. Phys. Lett. 307 (1999) 158.
[10] Y. Yang, S. Huang, H. He, A.W.H. Mau, L. Dai, J. Am. Chem. Soc. 121 (1999) 10832.
[11] R. Andrews, K. Jacques, A.M. Rao, et al., Chem. Phys. Lett. 303 (1999) 467.
[12] A.M. Rao, D. Jacques, R.C. Haddon, W. Zhu, C. Bower, S. Jin, Appl. Phys. Lett. 76 (2000) 3813.
[13] F. Rohmund, L.K.L. Falk, E.E.B. Campbell, Chem. Phys. Lett. 328 (2000) 369.
[14] H. Kind, J.-M. Bonard, C. Emmenegger, et al., Adv. Mater. 11 (1999) 1285.
[15] S. Fan, M. Chapline, N. Franklin, T. Tombler, A. Cassell, H. Dai, Science 283 (1999) 512.
[16] Z.F. Ren, Z.P. Huang, J.W. Xu, et al., Science 282 (1998) 1105.
[17] H. Cui, O. Zhou, B.R. Stoner, J. Appl. Phys. 88 (2000) 6072.
[18] C.J. Lee, J. Park, S.Y. Kang, J.H. Lee, Chem. Phys. Lett. 323 (2000) 554.
[19] C.J. Lee, J.H. Park, J. Park, Chem. Phys. Lett. 323 (2000) 560.
[20] C.J. Lee, J. Park, S.Y. Kang, J.H. Lee, Chem. Phys. Lett. 326 (2000) 175.
[21] X.X. Zhang, Z.Q. Li, G.H. Wen, K.K. Fung, J. Chen, Y. Li, Chem. Phys. Lett. 333 (2001) 509.
[22] Y. Kawashima, G. Katagiri, Phys. Rev. B 59 (1999) 62.
[23] A. Kasuya, Y. Sasaki, Y. Saito, K. Kohji, Y. Nishina, Phys. Rev. Lett. 78 (1997) 4434.
[24] W. Li, H. Zhang, C. Wang, et al., Appl. Phys. Lett. 70 (1997) 2684.