

Selective Growth of Straight Carbon Nanotubes by Low-Pressure Thermal Chemical Vapor Deposition

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Carbon nanotubes (CNTs) were grown by low-pressure thermal chemical vapor deposition using pure ethylene. It was found that straight CNTs, which were composed of bundled single- or double-wall CNTs and multiwall CNTs, were preferentially bridged between Fe nanoparticles under a low pressure of 100 Pa. Moreover, utilizing this method, we attempted to grow CNT bridges between patterned Ta electrodes. By nitriding the surface of the Ta electrodes, Fe nanoparticles with a moderate size were effectively formed, resulting in bridging CNTs between the electrodes. [DOI: 10.1143/JJAP.43.860]

KEYWORDS: carbon nanotube bridge, electrodes, low-pressure thermal chemical vapor deposition, ethylene, catalyst nanoparticles

1. Introduction

Recently, surface nanostructures and nanowires have attracted considerable attention from a wide range of scientific research fields, including nanoscale measurements of their electrical conductivity.¹⁾ Among them, single-wall and multiwall carbon nanotubes (SWNTs/MWNTs)²⁾ have been regarded as ideal nanowires that exhibit one-dimensional electronic systems.³⁾ Their intriguing electronic properties, combined with their small size, make carbon nanotubes (CNTs) excellent candidates for many technological applications, including field-effect transistors (FETs),⁴⁾ single-electron transistors (SETs)^{5,6)} and nanosensors.⁷⁾ The building blocks of these nanodevices consist of a single CNT bridged between two electrodes.^{8,9)} The method of dispersing CNTs on prepatterned electrodes has been mainly used to form the CNT-based building blocks. On the other hand, the method of direct synthesis of CNT bridges has been regarded as one of the most desirable routes to the realistic integration of such building blocks in terms of throughput and reproducibility. In the latter method, thermal chemical vapor deposition (T-CVD) with methane (CH₄) on catalyst-covered electrodes has been utilized for SWNT bridges.^{10–15)} However, the T-CVD with CH₄ requires a high pressure of approximately 10⁵ Pa and a high temperature of more than 900°C. For practical applications, it is desirable to adopt low-temperature and low-pressure processes which can facilitate the fabrication of the building blocks with a wide versatility. In this respect, T-CVD using hydrocarbon gases with low dissociative temperatures has prospects for such processes.^{16,17)}

In this study, by means of low-pressure T-CVD using pure ethylene (C₂H₄), we performed selective growth of CNT bridges between Fe nanoparticles. Under a low pressure of 100 Pa, it was found that straight CNTs were preferentially grown. High-resolution transmission electron microscopy (HRTEM) revealed that the resultant CNTs have two types of internal structures; bundled SWNTs or double-wall CNTs (DWNTs) and MWNTs. Moreover, the CNT bridges were grown on patterned Ta electrodes at 800°C. By nitriding the surface of the Ta electrodes, Fe nanoparticles with a

moderate size were effectively formed, resulting in bridging CNTs between the electrodes.

2. Experimental

Fe catalytic thin film with a thickness of 3 nm was deposited on SiO₂ (250 nm)/Si (100) substrates by sputtering at room temperature. CNTs were grown in a T-CVD setup which consists of a quartz tube, an electric furnace and gas flow control units. After the substrates were placed in the quartz tube, they were annealed for 30 min in a vacuum of below 9×10^{-1} Pa in the temperature range of 800 to 970°C to form Fe nanoparticles. The pure C₂H₄ (99.9%) gas as a source gas was introduced into the reactor under 50–170 Pa at a flow rate of 140–1500 sccm for 5–30 min. Regarding bridging straight CNTs between electrodes, prepatterned Ta pads (10 × 10 μm², 100 nm thick) on SiO₂/Si wafers were used as substrates. The distance of the trench between the Ta pads is 3 μm. To prevent the interface reaction between the Fe layer and Ta pads, the surface of the Ta pads was nitrided by N₂ plasma before Fe film deposition. N₂ plasma treatment was performed using a capacitively coupled plasma system under 10 Pa at 600°C for 30 min. Then, the substrate was treated by the same procedure as mentioned above. We utilized scanning electron microscopy (SEM) and HRTEM for the observations of the surface morphology and internal structure of resultant CNTs, respectively.

3. Results and Discussion

Figure 1(a) shows an SEM image of Fe nanoparticles formed on the substrate after annealing at 800°C for 30 min in vacuum. The average diameter and number density of the Fe nanoparticles were estimated to be 23 nm and 2×10^9 /cm², respectively. Figure 1(b) shows an SEM image of CNTs obtained after T-CVD at 800°C under 170 Pa for 5 min for the sample in Fig. 1(a). Under this condition, straight CNTs were observed at the center of Fig. 1(b). The diameter of the straight CNTs was smaller than that of the Fe nanoparticles. However, randomly curled CNTs (R-CNTs) predominantly grew over the substrate. The diameter of the R-CNTs was estimated to be approximately 25 nm, which coincides with that of the Fe nanoparticles. To perform selective growth of straight CNTs, growth parameters were optimized. With decreasing gas pressure and growth time,

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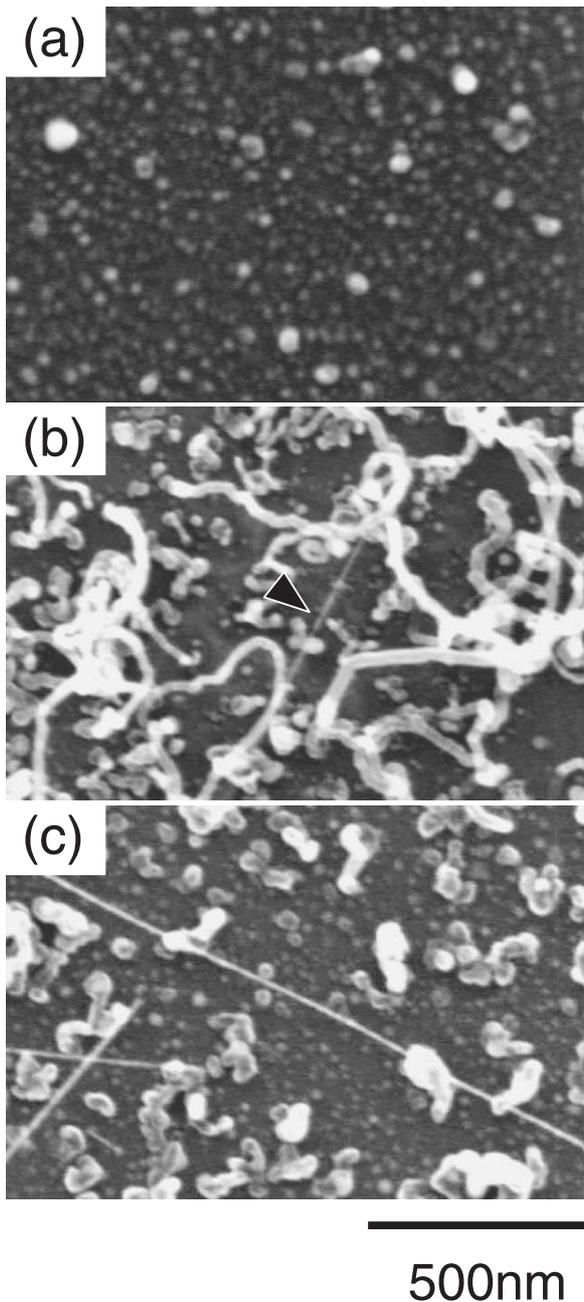


Fig. 1. SEM images of (a) Fe nanoparticles on the SiO₂/Si substrate after annealing at 800°C for 30 min, (b) CNTs grown at 800°C under 170 Pa and (c) straight CNTs selectively grown at 900°C under 100 Pa.

the number density and length of the R-CNTs were decreased. However, below a gas pressure of 50 Pa, the number of straight CNTs was also decreased. Beyond a growth temperature of 900°C, the number of R-CNTs was markedly decreased, and the length of the straight CNTs was shortened. Using the tendency of the CNT growth obtained above, we performed selective growth of straight CNTs by suppressing the R-CNT growth. Figure 1(c) shows an SEM image of the resultant CNTs grown at 900°C under 100 Pa for 5 min. It was clearly observed that the straight CNTs were bridged between Fe nanoparticles. The length of the CNTs was more than 3 μm.

Figure 2 shows an HRTEM image of R-CNTs. The R-CNTs had a typical MWNT structure with superior crystallinity. The number of graphite shells was estimated

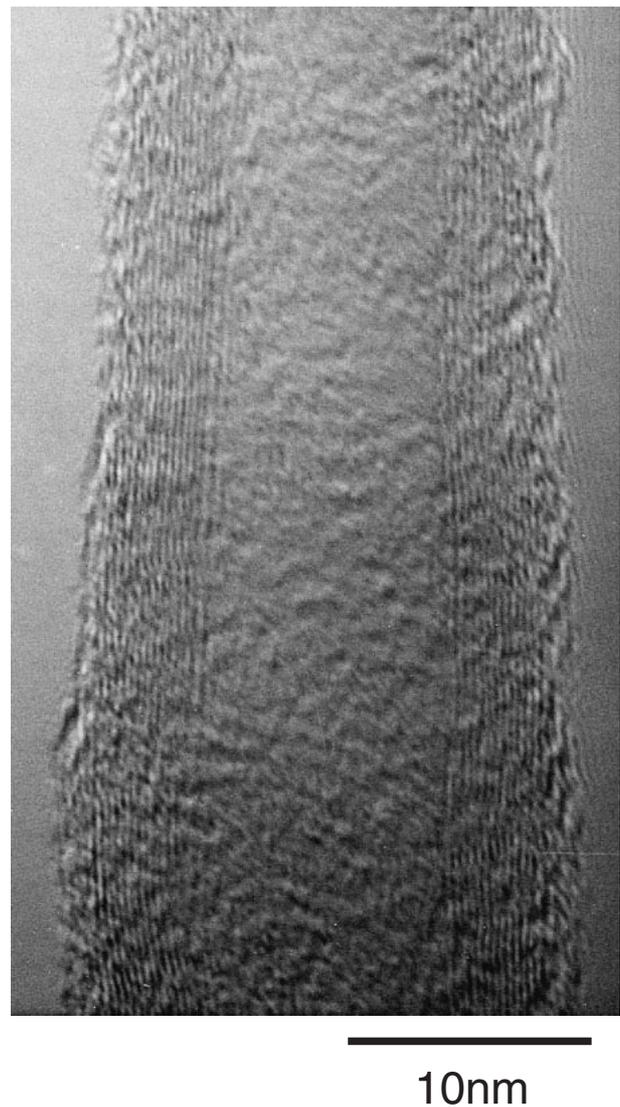


Fig. 2. HRTEM image of a R-CNT.

to be about 20. Figures 3(a) and 3(b) show HRTEM images of straight CNTs. It was found that the CNTs have two types of internal structures. One is a mixture of SWNTs and DWNTs which are bundled [Fig. 3(a)]. The branch from the bundled CNTs was clearly observed. The diameter of an individual CNT was approximately 2 nm. The other is a single MWNT with a diameter of 8–10 nm [Fig. 3(b)]. Figure 3(c) shows the selected area electron diffraction pattern of the MWNT. Graphite (002) and (004) spots were observed, indicating its superior crystallinity. Thus far, in the T-CVD of C₂H₄, it was reported that randomly curled bundled SWNTs could be grown from catalyst powders.¹⁶ In this aspect, this is the first observation of bundled SWNTs/DWNTs bridges between Fe nanoparticles grown by the T-CVD of C₂H₄.

Let us consider the mechanism of the selective growth of straight CNTs in our experiments. The processes that occur in the growth of the CNTs are (1) adsorption and dissociation of C₂H₄ molecules at the surface of Fe nanoparticles; (2) diffusion of C atoms into the Fe nanoparticles; and (3) precipitation of the C atoms at the surface of the Fe nanoparticles. Since it is likely that the decomposition of the supplied C₂H₄ molecules and the diffusion/

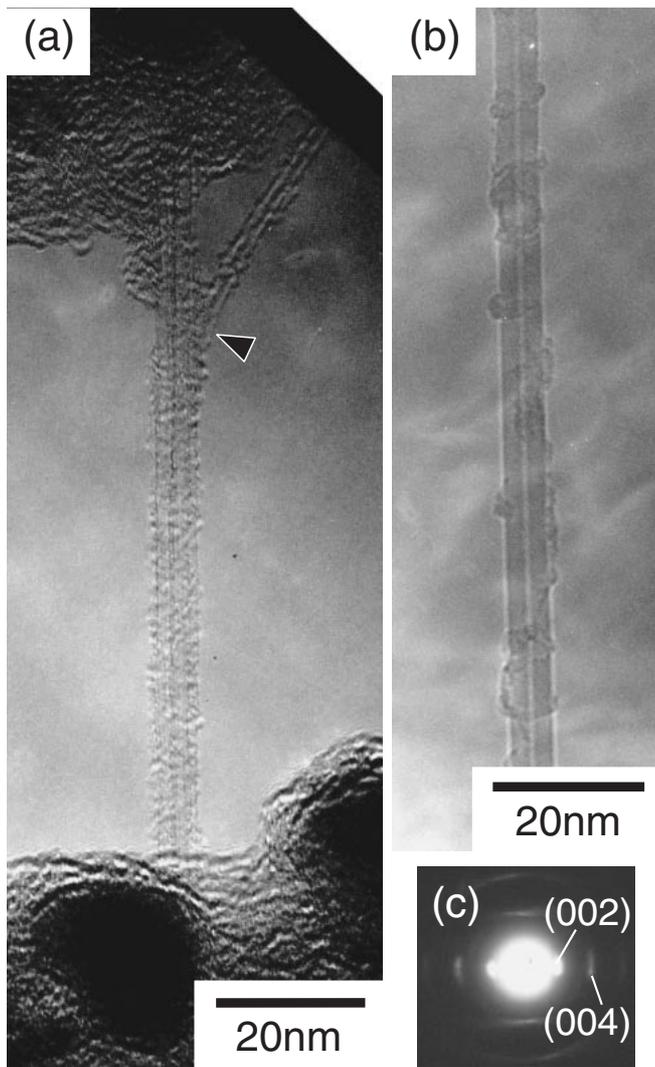


Fig. 3. HRTEM images of straight CNTs. (a) Bundled SWNTs/DWNTs. Black spheres at the lower part are Fe nanoparticles. (b), (c) MWNT and corresponding selected area electron diffraction pattern.

precipitation of the C atoms in the Fe nanoparticles readily occur at a relatively high growth temperature of 900°C, the growth is limited by the supply of feedstock. A decrease in both gas pressure and growth time corresponds to a decrease in the amount of supplied C₂H₄ molecules. Since the diameter of the straight CNTs (~8 nm) is smaller than that of the R-CNTs (~25 nm), the growth rate of the straight CNTs in length is much larger than that of the R-CNTs. Namely, the number of C atoms, *N*, which contributes to the growth of the straight CNTs with a unit length of 0.1 nm, is much smaller than that of R-CNTs. For example, for an R-CNT with a diameter of 25 nm and the number of shells of 18, *N* is 4160 atoms per 0.1 nm, while for a straight CNT with a diameter of 8 nm and the number of shells of 6, *N* is 450 atoms per 0.1 nm, where these MWNTs are assumed to have an armchair-type structure. Therefore, the supply of a moderate amount of C₂H₄ molecules promotes the selective growth of straight CNTs. This controllable growth is achieved by our low-pressure T-CVD method. Moreover, the diameter of the catalytic nanoparticles affects the selective growth of the straight CNTs. The diameter of the R-CNTs coincides with that of the catalytic nanoparticles,

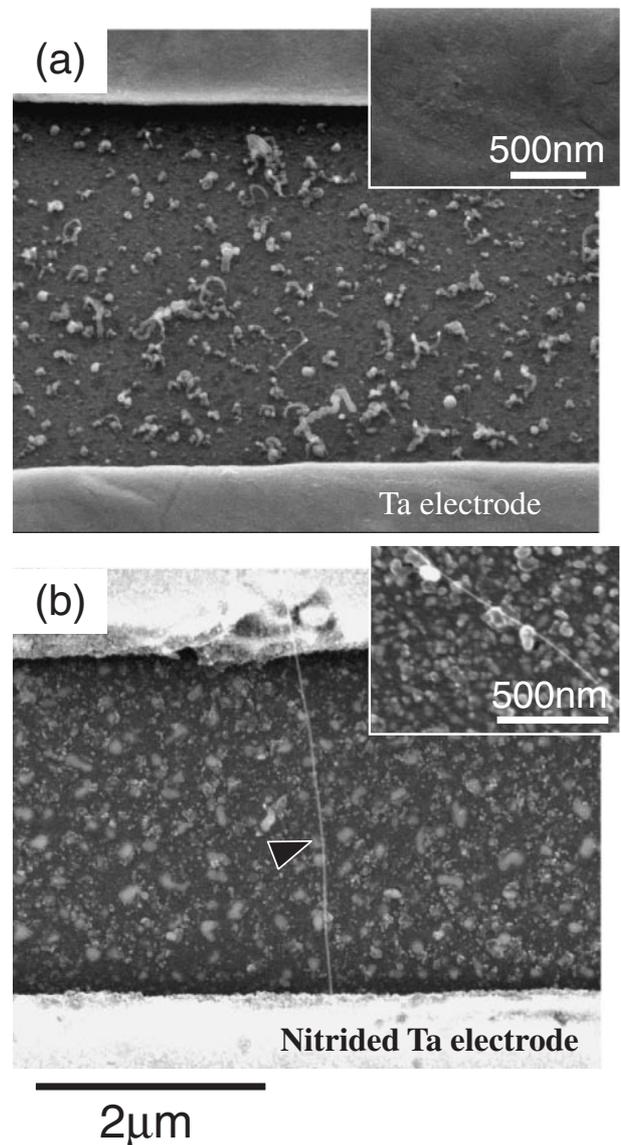


Fig. 4. SEM images of the samples after CVD growth for (a) Ta electrodes and (b) nitrided Ta electrodes. Top and bottom are the electrodes. Insets in both figures show SEM images of surfaces of the electrodes.

while that of the straight CNTs does not depend on that of nanoparticles. Namely, the growth rate of the R-CNTs decreases with increasing diameter of the catalytic nanoparticles, as demonstrated below. According to reports on SWNT growth using CH₄ gas,^{10–15)} the gas pressure for T-CVD is more than 500 times higher than that in this work. Differences between CH₄ and C₂H₄ T-CVD processes are as follows. First, the number of C atoms in a C₂H₄ molecule is twice that in a CH₄ one. Second, a C₂H₄ molecule can readily be dissociated at a lower temperature than that for CH₄ (equilibrium constant *K_p*: log₁₀*K_p* (727°C): -4.2 (2CH₄ ↔ C₂H₄ + 2H₂), -2.6 (C₂H₄ ↔ C₂H₂ + H₂)¹⁸⁾). These differences lead to the growth of straight CNTs under a low pressure with high controllability.

Utilizing the low-pressure CVD described above, we attempted bridging straight CNTs between patterned Ta electrodes using Ta pad/SiO₂/Si substrates. Figures 4(a) and 4(b) show SEM images of the samples after CVD without and with prenitridation treatment of substrates, respectively.

The CVD was performed at 800°C under 170 Pa for 5 min. In the case of Ta electrodes, no CNT bridges were observed. The inset in Fig. 4(a) shows a magnified SEM image of the Fe/Ta electrode, in which Fe nanoparticles were not observed. On the other hand, for the Ta electrodes treated by prenitridation, a straight CNT, whose diameter and length were below 10 nm and 4 μm, respectively, was observed to be bridged between electrodes. From the result on the growth of CNT bridges between Fe nanoparticles (Fig. 3), the resultant CNT appears to be an MWNT. As indicated in the inset in Fig. 4(b), Fe nanoparticles (average diameter of 46 nm) were formed on the surface of the electrodes. It is likely that while the bare Ta electrodes react with the Fe layer during CVD, the nitrided Ta layer acts as a reaction barrier against the formation of the Fe/Ta alloy layer at the interface, resulting in the effective formation of Fe nanoparticles. Moreover, we performed low-temperature growth of CNT bridges at 800°C. In Fig. 1(b), R-CNTs besides straight CNTs were dominantly grown at 800°C. On the other hand, using the nitrided Ta electrodes, straight CNTs were selectively grown without R-CNTs. Since the diameter of the Fe nanoparticles in Fig. 4(b) was twofold that in Fig. 1(b), it is likely that the growth rate of R-CNTs was markedly decreased, resulting in the prevention of R-CNT growth even at 800°C.

Our results demonstrate that MWNT bridges can be grown by T-CVD using C₂H₄ under a pressure as low as 100 Pa. Although the growth temperature (800–900°C) is still very high to fabricate CNT bridges between electrodes with a low melting point such as aluminum, there is a possibility of synthesizing CNT bridges in our low-pressure T-CVD using other carbon source gases such as C₂H₂ that can be decomposed at lower temperatures. In addition to SWNTs, aligned MWNTs have recently exhibited potential versatile applications such as SETs,¹⁹⁾ sensors²⁰⁾ and light sources.²¹⁾ Our method presented here can facilitate a low-pressure process for the fabrication of such MWNT-based building blocks.

4. Conclusions

We performed selective growth of straight CNT bridges between Fe nanoparticles by means of low-pressure T-CVD using pure C₂H₄. Under a low pressure of 100 Pa, it was found that the straight CNTs are preferentially bridged between the Fe nanoparticles. Resultant CNTs were composed of bundled SWNTs/DWNTs and MWNT. Moreover, CNT bridges were grown on patterned Ta electrodes. By nitriding the surface of the Ta electrodes, Fe nanoparticles

with a moderate size were effectively formed, resulting in bridging CNTs between the electrodes.

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- 1) For example, S. Hasegawa, I. Shiraki, F. Tanabe and R. Hobar: *Current Appl. Phys.* **2** (2002) 465.
- 2) S. Iijima: *Nature* **354** (1991) 56.
- 3) M. S. Dresselhaus, G. Dresselhaus and P. Avouris: *Carbon Nanotubes; Synthesis, Structure, Properties, and Applications* (Springer, Berlin, 2001).
- 4) S. J. Tans, A. R. M. Verschueren and C. Dekker: *Nature* **393** (1998) 49.
- 5) H. W. C. Postma, T. Teepen, Z. Yao, M. Grifoni and C. Dekker: *Science* **293** (2001) 76.
- 6) N. Yoneya, E. Watanabe, K. Tsukagoshi and Y. Aoyagi: *Appl. Phys. Lett.* **79** (2001) 1465.
- 7) Y. Cui, Q. Wei, H. Park and C. M. Lieber: *Science* **293** (2001) 1289.
- 8) A. Bachtold, P. Hadley, T. Nakanishi and C. Dekker: *Science* **294** (2001) 1317.
- 9) S. J. Wind, J. Appenzeller, R. Martel, V. Derycke and P. Avouris: *Appl. Phys. Lett.* **80** (2002) 3817.
- 10) J. Kong, A. M. Cassell and H. Dai: *Chem. Phys. Lett.* **292** (1998) 567.
- 11) J. Kong, H. T. Soh, A. M. Cassell, C. F. Quate and H. Dai: *Nature* **395** (1998) 878.
- 12) H. T. Soh, C. F. Quate, A. F. Morpurgo, C. M. Marcus, J. Kong and H. Dai: *Appl. Phys. Lett.* **75** (1999) 627.
- 13) N. R. Franklin and H. Dai: *Adv. Mat.* **12** (2000) 890.
- 14) Y. Homma, T. Yamashita, P. Finnie, M. Tomita and T. Ogino: *Jpn. J. Appl. Phys.* **41** (2002) L89.
- 15) Y. Homma, Y. Kobayashi, T. Ogino and T. Yamashita: *Appl. Phys. Lett.* **81** (2002) 2261.
- 16) J. H. Hafner, M. J. Bronikowski, B. R. Azamian, P. Nikolaev, A. G. Rinzler, D. T. Colbert, K. A. Smith and R. E. Smalley: *Chem. Phys. Lett.* **296** (1998) 195.
- 17) P. M. Campbell, E. S. Snow and J. P. Novak: *Appl. Phys. Lett.* **81** (2002) 4586.
- 18) *Thermochemical Table* (JANAF, 1971) 2nd ed.
- 19) K. Ishibashi, D. Tsuya, M. Suzuki and Y. Aoyagi: *Appl. Phys. Lett.* **82** (2003) 3307.
- 20) L. Valentini, I. Armentano, J. M. Kenny, C. Cantalini, L. Lozzi and S. Santucci: *Appl. Phys. Lett.* **82** (2003) 961.
- 21) P. Li, K. Jiang, M. Liu, Q. Li, S. Fan and J. Sun: *Appl. Phys. Lett.* **82** (2003) 1763.