



Controlled assembly of single SWNTs bundle using dielectrophoresis

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Abstract

We present a mass productive and reproducible assembly technique of a single bundle of single-walled carbon nanotubes (sb-SWNTs) using dielectrophoresis (DEP). Gold electrodes with 10 gaps made via microlithography were used to align the carbon nanotubes (CNTs). The magnitude and type of applied electric field were investigated to verify their effects on CNT assembly. The optimum assembling conditions in which sb-SWNTs could be positioned at a desired site were experimentally identified, and the characteristics of the assembled sb-SWNTs were evaluated from AFM, Raman spectroscopy, and I - V curve. This assembly method has potential for applications, such as gas sensors or electronic devices.

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1. Introduction

Carbon nanotubes (CNTs) have attracted strong attention since their discovery in 1991 owing to their

unique electrical and mechanical properties [1–3]. Possessing high aspect ratio, strong mechanical strength, and high electrical and thermal conductivity, they are considered outstanding materials. Metallic or semiconducting CNTs have been utilized to fabricate electronic devices, such as field-effect transistors, memory, chemical and mechanical sensors, and measurement probes [4–8].

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For the real application of CNT devices, it is very significant not only to align CNTs at the desired site but also to control the number of CNTs at that position, because many CNT-based devices are very sensitive to the number and the position of the assembled CNTs.

Several approaches have been used to arrange each nanotube in the proper position and desired formation including direct growth and manual attachment of CNTs on an electronic circuit. The direct growing technique, however, requires high temperature and patterning of very tiny catalysts on the exact point [9]. Furthermore, the uniform growth of CNTs for each catalyst is extremely difficult. Meanwhile, manual attachment is regarded as commercially unviable because of long handling time, expensive apparatus, a vacuum environment, and difficulty of handling the SWNTs. It has also been difficult to assemble CNTs over a large area with high speed [10].

Recently, some useful and efficient assembly methods have been devised, wherein chemical surface treatment, a magnetic field, or an electric field is employed for assembling CNTs at designed positions [11–13]. One of these methods, dielectrophoresis (DEP), which uses an electric field, is a very useful technique to control the assembly of nanotube bundles on an electrode [14–16]. Meanwhile, two important results about fundamental study of the nanotube dielectrophoresis and a large scale assembly technique of the nanotube by using dielectrophoresis have been reported by Krupke et al. [17,18]. The DEP technique has advantages in that the position and number density of aligned CNTs can be controlled by adjusting the electric field. Several assembling methods using multi-walled carbon nanotubes (MWNTs) under an electric field using DEP force have been reported [14,15]. Even though the number of carbon nanotubes could be controlled, most of the assembled nanotubes had metallic properties. However, MWNT has lower sensitivity than SWNT.

SWNTs, meanwhile, are likely to be strongly aggregated and exist in a bundled form in spite of purification and dispersing processes. Even though nanotubes in a bundled form apparently have metallic properties, nanotubes with semiconducting properties are generally included into the

single bundle of single-walled carbon nanotubes (sb-SWNTs). If necessary, the metallic nanotubes in sb-SWNTs could be selectively removed by an electrical burning method for the fabrication of sensors composed of semiconducting CNTs [16]. These assembled sb-SWNTs, therefore, could be available to nano devices, because sb-SWNTs have versatile properties. Although several studies have reported on sb-SWNT assembly by the DEP method, a reproducible method of controlling the number density of CNTs at a desired location and determination of the optimum conditions for CNT alignment are still required [19,20].

Here, we report a repeatable and reproducible assembling technique of sb-SWNTs at a designed position and also suggest optimum conditions to control the number of sb-SWNTs between electrode gaps. In addition, the position and the shape of aligned sb-SWNTs could be tuned by adjusting the electric field line. The diameter of the sb-SWNTs and the number of SWNTs in sb-SWNTs are inferred from the measured results of AFM and Raman spectroscopy. I - V curve and Raman spectroscopy results demonstrated that the assembled sb-SWNTs had semiconducting SWNTs.

2. Experimental setup

In this experiment, Au electrode arrays with 10 gaps of round shape, as shown in Fig. 1(a), were used for the electrical contact of nanotubes between the Au electrode gaps, the gap distance was 4 μm . The Au microelectrodes were prepared by optical lithography on a silicon wafer. First, 200 nm SiO_2 was deposited onto the silicon wafer to insulate between the metal electrode and the wafer. Second, a 50-nm gold layer was built onto the SiO_2 layer to serve as an electric conductor.

The SWNT bundles were prepared by laser ablation. The nanotubes were ultrasonically dispersed in dichloroethylene (DCE) solvents in order to unfasten the nanotube bundles.

The solutions of SWNTs (0.5 μl) were dropped on the electrode gap using a pipet. AC (alternating current) electric fields from 1 to 10 V at a constant frequency of 5 MHz were applied on the electrode for the DEP experiment. In addition,

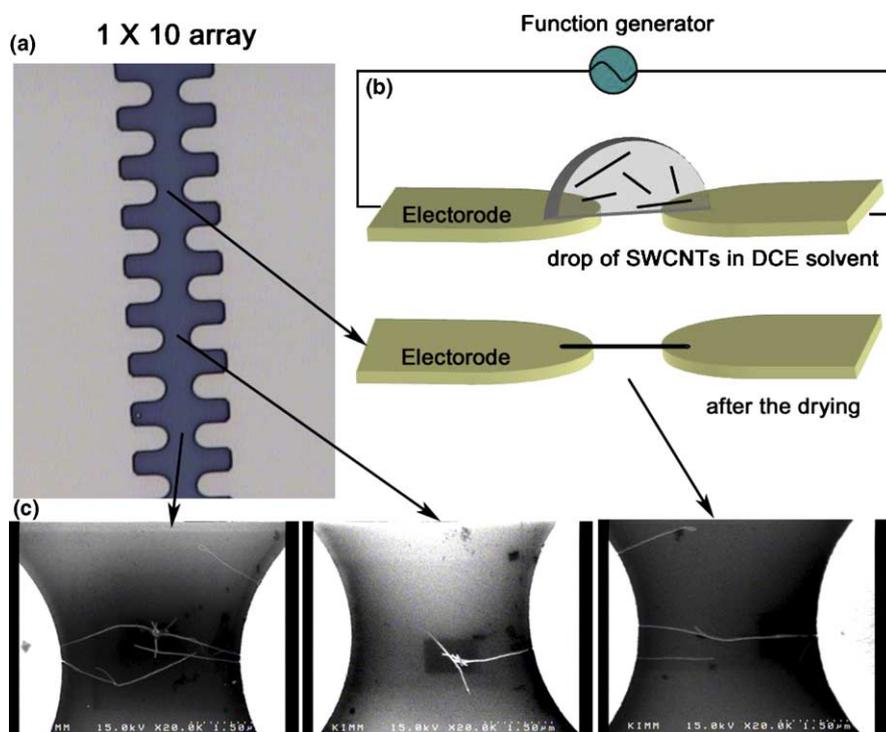


Fig. 1. (a) Optical image of electrode array with 10 round-shaped gaps. (b) Schematic of the experiment for SWCNT assembly across the electrode gap. (c) SEM images of gap on indicated position (4 μm gap distance, at 3 V).

we investigated whether the number of sb-SWNTs could be controlled by changes of the types of electric field. A function generator and an oscilloscope were used for the electric field generation and the signal check, respectively. All experiments were carried out at room temperature for several minutes. Scanning electron microscopy (SEM, Hitachi S-4100) was used to verify the number of sb-SWNTs. The diameter of sb-SWNTs was calculated from the results of AFM (Model: PSIA Co, XE-200) and Raman spectroscopy with a 514.5 nm Ar-ion laser (Ranishaw 1000). A signal analyzer (HP4145B) was used to measure the I - V curve.

3. Results and discussion

In the DEP experiment, the charge distribution at the interface between two materials of different conductivity and/or permittivity is important. In

the presence of an applied electric field, if a non-uniform electric field exists, the field strength and the force acting on each side of the particle will be different, causing the particle to move with respect to the medium. When a polarizable object is subjected to an electric field, a dipole moment is induced. The nanotubes with high aspect ratio are largely affected by the DEP forces because of the increase in their polarization. If there are particles that are larger than the nanotubes, the large particles are first attracted between the electrodes. However, in our experiments, there were no large particles such as impurities between the electrodes, because we used high purity SWNTs. In addition, DEP force depends on both the particle size and the gradient of the electric field, which is determined by the geometry of the electrode. It is known that CNTs are oriented and aligned along the electric field line [21].

While the CNTs undergo various forces including gravity, Brownian motion, and DEP force, we

focus on DEP force in the present experiment as Brownian motion and gravity are negligible. Attraction of CNTs at the electrode could be explained by the theoretical formula for a DEP force [21]. Dielectrophoretic force can be written as

$$F_{\text{DEP}} = \frac{1}{4} v \text{Re} \left[\frac{\tilde{\epsilon}_p - \tilde{\epsilon}_m}{\tilde{\epsilon}_p + 2\tilde{\epsilon}_m} \right] \nabla |E|^2, \quad (1)$$

where E is the electric field and v is the dimensional constant of the particle. $\tilde{\epsilon}_m$ and $\tilde{\epsilon}_p$ are the complex permeability of the medium and the particle, respectively. In this case, the particle means the CNT and the medium is DCE (dichloroethylene) [21].

$$\tilde{\epsilon}_m = \epsilon_m - j \frac{\sigma_m}{\omega}, \quad \tilde{\epsilon}_p = \epsilon_p - j \frac{\sigma_p}{\omega}, \quad (2)$$

where j is a complex number, σ is conductivity, and ω is applied frequency.

In the case of a sharp electrode, shown in our previous work, the electric field was concentrated on the sharp edge and electric field line is more rapidly changed at that region. When the CNT is attracted to this region, the moving speed reaches a maximum value at the edge point. For this reason, it is difficult to stable positioning at sharp edge [22]. Therefore, CNTs are likely to pass away rather than to stay at the sharp location of the gap. Hence, we speculated that it would be difficult to find a

location to situate the CNT. In the case of a round electrode, the electric field gradient has a smooth change near the round edge. This means that the moving speed of the CNT slows down near the round edge. In Eq. (1), we can find $|\Delta E|^2 \approx 0$ at the middle area of the round edge. There is little DEP force around this area. Therefore, the round shape would be more preferable to assemble the nanotube compared with the sharp shape, as we could obtain a wider stable area to fix the CNT. For this reason, we designed round-shaped electrodes and then simulated the electric field of the electrode using a commercial FEMLAB program.

A typical result of a two-dimensional simulation of an electrical field onto an electrode gap is shown in Fig. 1(a). The results of Fig. 2 show that alignment is dependent on the direction of the electric field, as anticipated. Fig. 2(a) is the simulation result for the designed round-shape electrode. Fig. 2(b) is an SEM image of the sb-SWNT aligned and bent along the electric field line, where the length of the SWNT is longer than the electrode distance. If we were to use a multi-walled carbon nanotube, the nanotube would not be bent due to its high stiffness. In contrast, the sb-SWNTs can be well aligned and bent along the electric field line because of their flexibility. In addition, the position of the aligned sb-SWNTs can be controlled according to the change of the electric field line.

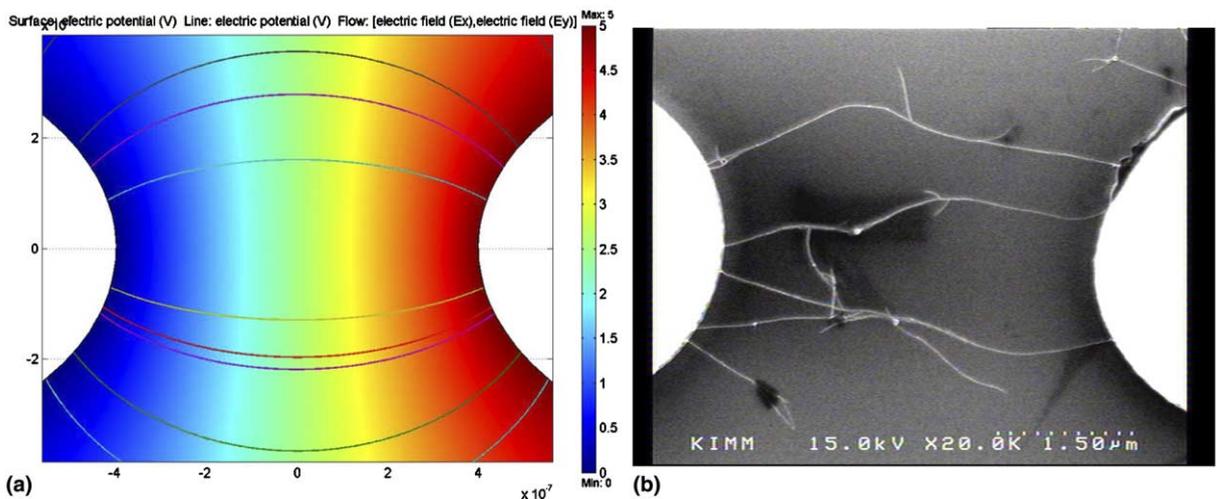


Fig. 2. (a) Simulation result of a electrode using a FEMLAB program. (b) SEM image of SWCNT along the electric field line connected between electrodes.

Fig. 1(b) shows a schematic view of application of the electric field on the electrode using a function generator. A solution of the well-dispersed sb-SWNTs ($0.5 \mu\text{l}$) was dropped on the electrode gap using a pipet. After drying the solvents and removing the electric field, well-aligned sb-SWNTs connected between the electrodes were obtained without other particles or impurities. Fig. 1(a) shows an optical image of 1×10 gold electrode arrays used in our experiment.

As shown in Fig. 1(c), the sb-SWNTs connected the gaps between electrodes at fixed ac 3 V. From this test, we assessed the assembling yield between the 1×10 electrode array, and it was about 50–70%.

Raman spectroscopy and AFM were used to determine the average number of single SWNTs (s-SWNT) in the individual sb-SWNTs connected on each electrode gap. Raman spectrum bands of 1565.8 and 1589.7 cm^{-1} in Fig. 3(a) indicate that both metallic and semiconducting CNTs are present in each sb-SWNT. Using the 186.01 cm^{-1} band

of the RBM mode, shown in the inset of Fig. 3(a), the diameter of individual s-SWNT, which is 1.30 nm , could be estimated [23]. Fig. 3(c) is an AFM image and line profile of sb-SWNT. From these AFM images, it could be shown that the diameter of the sb-SWNT was 6.65 nm and each sb-SWNT had an average number of five s-SWNTs. Electrical properties of single MWNT (s-MWNT) and sb-SWNT were measured using an I - V curve. As shown in Fig. 3(b), metallic and semiconducting properties appeared in the s-MWNT and sb-SWNT, respectively.

We controlled the number of assembled sb-SWNTs via two factors: the magnitude of the applied voltage and the electric field type, such as AC only, DC (direct current) biased AC with a capacitance and resistor, and AC with a capacitance, as suggested in a recent paper [15]. The purpose of the electric field type test is to find optimum conditions which single CNT can be assembled on the electrode. The SEM images of Fig. 4 show that

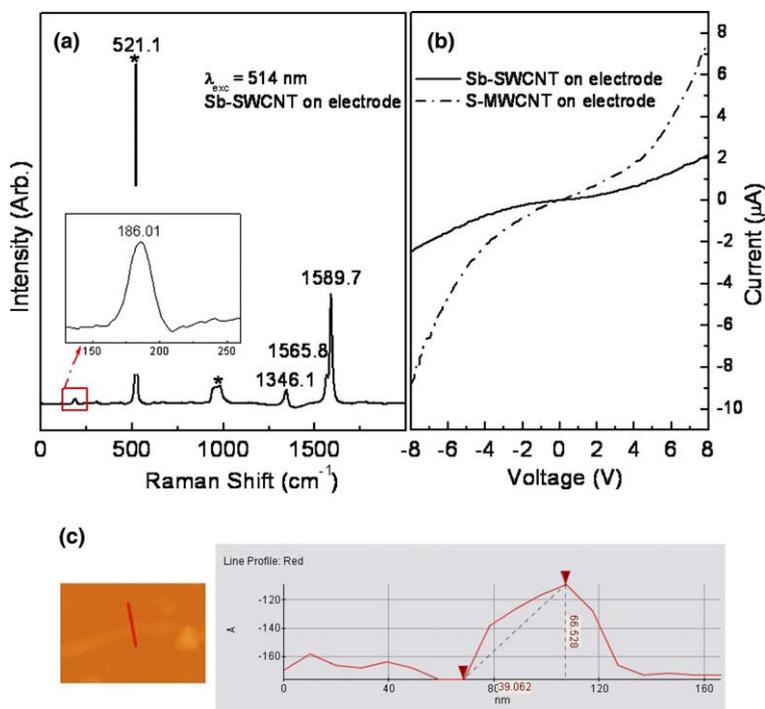


Fig. 3. (a) Micro-Raman spectroscopy of sb-SWNTs obtained at room temperature, inset indicates RBM mode analysis for single diameter of SWNT. Asterisk denotes Si peak generated from the substrate of the electrode. (b) I - V curve of CNT device, showing behavior indicative of a semiconducting (sb-SWNT) and metallic (s-MWNT) (c) AFM image of sb-SWNT and line profile.

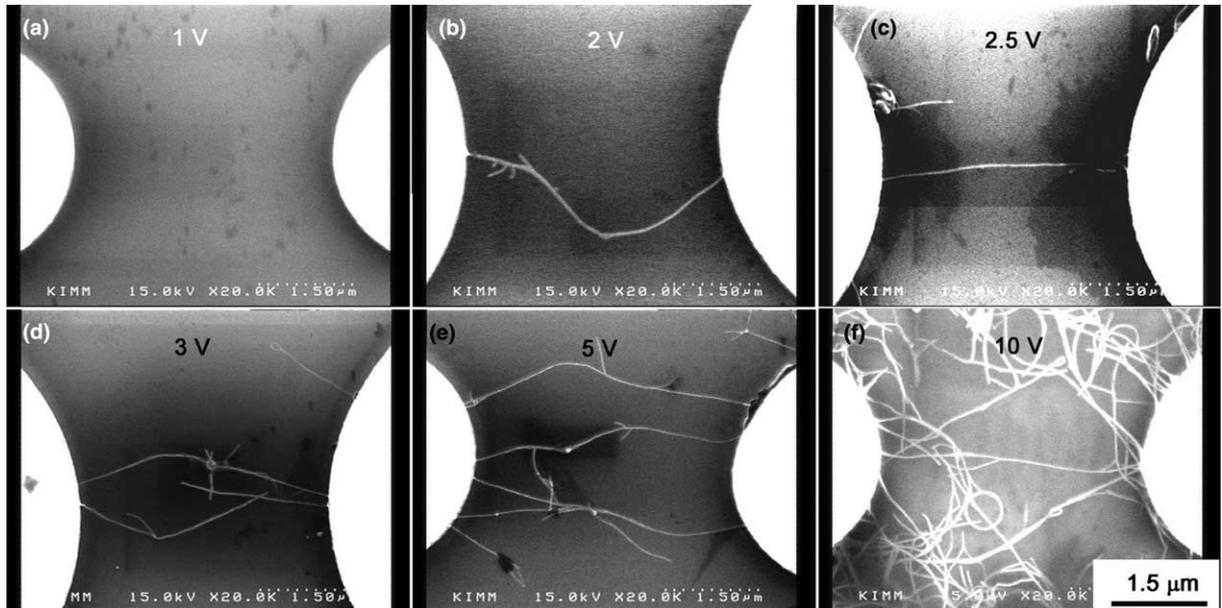


Fig. 4. SEM images of SWCNT deposition as a function of the varying of voltage magnitude: (a) 1 V, (b) 2 V (c) 2.5 V, (d) 3 V, (e) 5 V, (f) 10 V.

alignment and the number of sb-SWNTs can be tuned by changing ac electric fields from 1 to 10 V at a constant frequency of 5 MHz. It was observed that the number of sb-SWNTs increased with the applied ac voltage. We found that below one volt sb-SWNTs were not connected in any region of the 1×10 electrode gap arrays, as shown in Fig. 4(a). From Fig. 4(b)–(d), we see that sb-SWNTs having a number of 1–3 between individual electrode gaps could be obtained between 2 V and 3 V. The optimum voltage for the alignment of sb-SWNTs having a number of only one is

approximately 2 V. When an electric field above 3 V was applied to the electrodes, the number of aligned SWNTs was further increased.

However, when the applied voltage was around 10 V, random network structures composed of sb-SWNTs were fabricated, as shown in Fig. 4(f), because of the high density of sb-SWNTs. In this case, most of the sb-SWNTs were located around the gap and their number could not be controlled in this regime.

Another important assembling factor for individual nanotube alignment is the type of applied

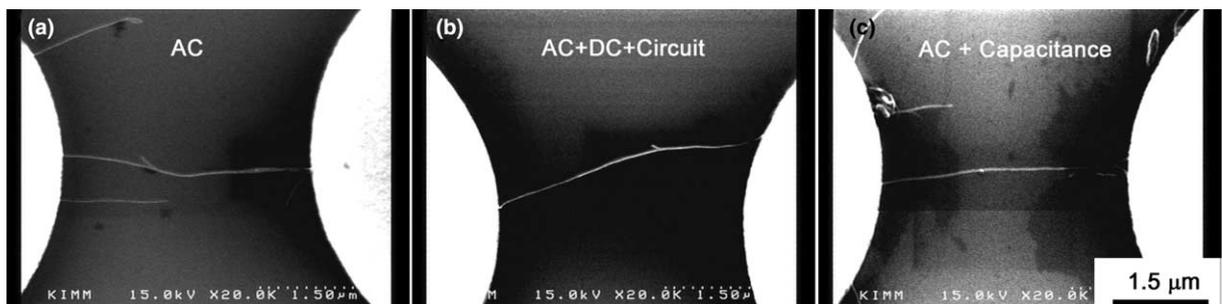


Fig. 5. SEM images of SWCNT deposition as a function of the varying of voltage type: (a) AC, (b) AC+DC+Circuit, and (c) AC+Capacitance. Constant voltage of 2.5 V was applied.

electric field. To compare the results of mixed electric type with those from application of only AC 2.5 V, shown in Fig. 5(a), we applied different types of electric fields, AC+DC+Circuit (Resistance (1 G Ω)+Capacitance (2.2 μ F)) (Fig. 5(b)) and AC+Capacitance (Fig. 5(c)), to the electrode gaps, respectively. Assembly trends of sb-SWNTs for these electric types are very similar, as shown in Fig. 5. Under the same conditions, when we applied the 5 V, we could see an increase in the number of connected sb-SWNTs without a large difference in tendency for each electric type condition. As such, these results imply that the assembly of sb-SWNTs under DEP is mainly affected by the magnitude of applied voltage rather than the applied voltage type.

4. Conclusions

In summary, we report the effects of the magnitude and types of electric field on the control of the number density of sb-SWNTs between electrode gaps and suggest the optimum assembling conditions of sb-SWNTs using DEP force. sb-SWNTs with a number density of one to three could be successfully bridged between gold electrode gaps when an electric field of 2–3 V was applied at a frequency of 5 MHz. The density of aligned nanotubes mainly depends on the magnitude of applied electric field. The position and shape of the aligned sb-SWNTs were affected by the electric field. The average diameter of the sb-SWNT connected between the gaps was around 6.65 nm and each bundled nanotube was composed of an average of five SWNTs. Also, the position of assembled nanotubes could be controlled, if we controlled the electric field when designing the electrode. This technique will be a useful method for several potential applications such as gas sensors or other electronic devices.

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References

- [1] S. Iijima, *Nature* 354 (1991) 56.
- [2] H. Dai, *Appl. Phys.* 80 (2001) 29.
- [3] R. Saito, G. Dresselhaus, M.S. Dresselhaus, *Physical Properties of Carbon Nanotubes*, Imperial College Press, London, 1998.
- [4] P.L. McEuen, M.S. Fuhrer, H. Park, *IEEE Trans. Nanotechnol.* 1 (2002) 78.
- [5] R.H. Baughman, A.A. Zakhidov, W.A. de Heer, *Science* 297 (2002) 787.
- [6] P.G. Collins, P. Avouris, *Sci. Am.* 62 (2000).
- [7] H. Dai, *Phys. World.* 3 (2000) 43.
- [8] H. Dai, J.H. Hafner, A.G. Rinzler, D.T. Colbert, R.E. Smalley, *Nature* 384 (1996) 147.
- [9] Y.T. Jang, J.-H. Ahn, B.-K. Ju, Y.-H. Lee, *Solid State Commun.* 126 (2003) 305.
- [10] M.F. Yu, O. Lourie, M.J. Dyer, K. Moloni, T.F. Kelly, R.S. Ruoff, *Science* 287 (2000) 637.
- [11] K. Yamamoto, S. Akita, Y. Nakayama, *J. Phys D* 31 (1998) L34.
- [12] D.P. Long, J.L. Lazorcik, R. Shashidhar, *Adv. Mater.* 16 (2004) 814.
- [13] S.G. Rao, L. Huang, W. Setyawan, S. Hong, *Nature* 425 (2003) 36.
- [14] J. Suehiro, G. Zhou, M. Hara, *J. Phys. D* 36 (2003) L109.
- [15] J. Chung, K.-H. Lee, J. Lee, R.S. Ruoff, *Langmuir* 20 (2004) 3011.
- [16] P.G. Collins, M.S. Arnold, P. Avouris, *Science* 292 (2001) 706.
- [17] R. Krupke, F. Hennrich, H.B. Weber, M.M. Kappes, H.V. Löhneysen, *Nano Lett.* 3 (2003) 1019.
- [18] R. Krupke, F. Hennrich, M.M. Kappes, H.V. Löhneysen, *Nano Lett.* 4 (2004) 1395.
- [19] X.Q. Chen, T. Saito, H. Yamada, K. Matsushige, *Appl. Phys. Lett.* 78 (2001) 3714.
- [20] R. Krupke, F. Hennrich, H.B. Weber, D. Beckmann, O. Hampe, S. Malik, M.M. Kappes, H.V. Löhneysen, *Appl. Phys. A* 76 (2003) 397.
- [21] T.B. Jones, *Electromechanics of Particles*, Cambridge University Press, 1995.
- [22] H.W. Lee, S.H. Kim, Y.K. Kwak, C.S. Han, in: *Proc. ASME IMECE 2004-61602*, 2004.
- [23] J.-L. Sauvajol, E. Anglaret, S. Rols, L. Alvarez, *Carbon* 40 (2002) 1697.