



# Dielectrophoretic deposition of carbon nanotubes: The role of field frequency and its dependence on solution conductivity



Ali Kashefian Naieni\*, Alireza Nojeh

Department of Electrical and Computer Engineering, The University of British Columbia, Vancouver, BC V6T 1Z4, Canada

## ARTICLE INFO

### Article history:

Received 6 December 2012

Received in revised form 23 August 2013

Accepted 2 September 2013

Available online 15 September 2013

### Keywords:

Dielectrophoresis

Carbon nanotube

Deposition from solution

Frequency

Solution conductivity

Electrothermal force

## ABSTRACT

Dielectrophoretic deposition is ubiquitous in the fabrication of nanoscale devices and, in particular, carbon nanotubes from solutions. The physical properties of the solution play a major role in determining the nanotube patterns deposited using this technique; the non-uniform temperature profile generated by the passage of current can create forces in the solution, which result in agitations and can interfere with the dielectrophoresis force.

The forces that induce movement in the solution, as well as the dielectrophoresis force, all vary with frequency in different manners. In this work, experiments and simulations are used in order to investigate the interplay between the solution conductivity and the frequency of the applied voltage, and their effects on the deposition patterns. We demonstrate that changes in the frequency affect solutions with different physical properties differently: while the frequency directly influences the number of deposited carbon nanotubes when using solutions with low conductivity, it is almost of no consequence in the case of solutions that include surfactants and thus have a higher conductivity.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Despite the promising properties of carbon nanotubes (CNTs), reproducibility in fabrication still remains a challenge and a bottleneck for many applications. Dielectrophoresis (DEP) is widely used for the deposition of a CNT or a collection of CNTs between two electrodes [1–4]. DEP offers several advantages: it is performed at low temperatures and enables a high level of control over the location and direction of the deposited nanotubes. Moreover, since solutions containing different types of CNTs are readily available, DEP naturally allows for the fabrication of devices based on specific CNT types.

Nonetheless, DEP results are not always fully reproducible. The role of the various parameters involved such as the amplitude and frequency of the applied voltage, the shape of the electrodes, the duration of experiment, and the properties of the solution, has formed the subject of several previous studies [5–10]. However, important questions still remain.

Current methods for the preparation of aqueous suspensions of CNTs can result in solutions with a wide range of conductivities. Pure CNTs being hydrophobic, the main processes available for suspending them in water involve the addition of surfactant materials [11] or the pre-treatment of the CNTs [12]. Depending on the type and amount of surfactant added, the resulting solution can have

different physical properties that affect the DEP process, including electrical conductivity, which can have a significant effect. However, this effect is not fully understood yet and, in fact, has often been neglected.

The application of an alternating voltage between electrodes immersed in a CNT solution leads to a DEP force being exerted on the CNTs. Depending on the permittivity and conductivity of the CNTs and those of the solution, the DEP force will either attract the CNTs to regions where the gradient of the field is the greatest (the gap between the electrodes) or repel them. Another phenomenon occurs due to the heat produced by the current passing through the solution because of the applied voltage. The non-uniform temperature profile leads to a non-uniform distribution of the permittivity and conductivity of the solution, both of which are functions of temperature. Under the applied electric field, a so-called electrothermal force is created, which produces movement in the solution. The magnitude and direction of this force, and the velocity of the resulting movement of the solution, depend on the physical properties of the medium as well as the frequency of the applied electric field [13–15].

A limited number of reports exist on the effect of the movement in the solution during the DEP deposition of CNTs. Using a numerical approach, Lin et al. demonstrated that this movement affects the semiconducting CNTs considerably [16]. In a highly insightful simulation study, Burg et al. adopted a two-dimensional electrokinetic framework in order to evaluate the effect of different forces resulting from the non-uniformity of the temperature profile

\* Corresponding author.

E-mail address: [alikh@ece.ubc.ca](mailto:alikh@ece.ubc.ca) (A. Kashefian Naieni).

around the electrodes [17]. They demonstrated that the electrothermal force is the dominant volumetric force on the solutions containing surfactants in the frequency ranges relevant to DEP. Moreover, they showed that the direction of this force depends on the frequency. Although both of the above works investigated the forces affecting the movement of the CNTs at different frequencies, their focus was on the dependence of the movement of the solution on the frequency, rather than its effect on the deposition pattern of the CNTs. Moreover, the simulated frequencies in these works were typically not within the frequency ranges used in DEP experiments on nanotubes.

We previously investigated the simultaneous effects of the electrothermal and DEP forces on CNTs and the resulting deposition pattern at a single frequency for solutions with different levels of conductivity [18]. It was observed that the electrothermal force cannot be neglected in solutions containing surfactants. In addition, the effect of this force does not depend strongly on the percentage of surfactant in stable nanotube solutions; however, it is drastically less pronounced for solutions without surfactant. For solutions with one weight percent (wt%) sodium dodecylbenzene sulfonate (SDBS), which is typical for CNT deposition, the electrothermal force is the dominant player in the long-range drift of the CNTs, and affects the deposition pattern dramatically compared to the situation in the solution with no surfactant.

An important question here is how the effects of the two main forces – the DEP force and the electrothermal force – evolve with respect to each other as the frequency of the applied voltage is varied. This is a critical issue that requires detailed investigation. In this article, we use experiments and finite element simulations to investigate the interplay between these two forces at different frequencies. We show that there exists a threshold frequency beyond which the number of deposited CNTs bridging the electrodes reduces drastically. For low-conductivity solutions (those made using pre-treated nanotubes), this threshold falls within the frequency range used in practice, whereas in high-conductivity solutions (those including surfactants), it is orders of magnitude higher.

## 2. Methodology

CNTs are hydrophobic in nature. The two primary methods for suspending nanotubes in water are using surfactants, such as SDBS, or using pre-treatment to functionalize the CNTs. Although both methods result in stable nanotube solutions, the conductivities of the resulting solutions are considerably different.

The concentration of CNTs in a water–surfactant solution depends on the surfactant concentration, which, on the other hand, determines the conductivity of the solution. However, in order to be able to investigate the effect of solution conductivity on the deposition patterns of the CNTs at various frequencies, it is necessary to decouple it from the effect of CNT concentration; one needs to prepare solutions with different conductivities, but identical in other aspects.

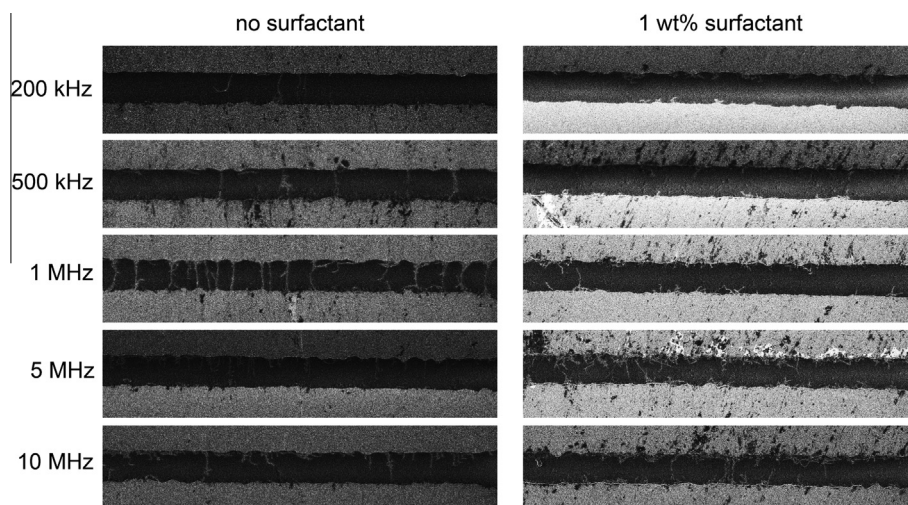
To accomplish this, we used a surfactant-free single-walled CNT solution, commercially available from NanoLab Inc. [19], in which the nanotubes are carboxylated prior to suspension in water. The nanotubes had lengths in the range of 1–5  $\mu\text{m}$  and an average diameter of 1.5 nm. The initial concentration of the solution was 1 g/l. The nanotube solution was diluted to the desired concentration. For each sample with a certain concentration of CNTs, two solutions with 0 and 1 wt% SDBS were prepared. Each of the solutions was ultrasonicated for 5 min.

Although the surfactant molecules interact with the CNTs, they do not change the CNT concentration because the CNTs are already suspended. The role of the SDBS here is merely to change the conductivity of the solution. It is noteworthy that, since the SDBS molecules attach to the nanotubes through Van der Waals forces, they do not affect the physical properties of the nanotubes.

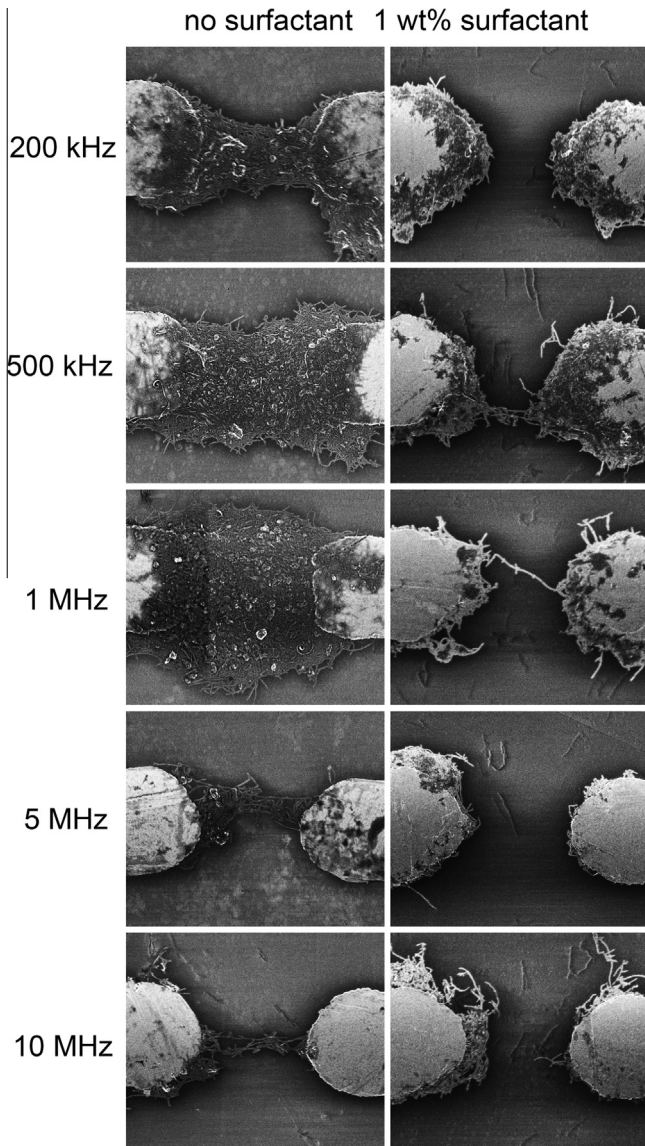
The electrodes were fabricated using photolithography and electron beam evaporation, followed by lift-off in acetone, on a p-doped silicon wafer with a 2- $\mu\text{m}$ -thick thermal oxide on the surface. The evaporated metal layers consisted of a 50-nm-thick palladium layer over a 20-nm-thick chromium layer for adhesion. Two types of electrodes were used in the experiments. In the first type, the electrodes were 4  $\mu\text{m}$  in width and had a curved border, with a gap of 4  $\mu\text{m}$  between opposite electrodes; these will be called narrow electrodes from now on. The second type consisted of electrodes 40  $\mu\text{m}$  wide and 4  $\mu\text{m}$  apart from each other; these will be called wide electrodes. The samples were cleaned using acetone, methanol and deionized (DI) water prior to DEP experiments.

The DEP experiments were conducted by applying a 5-V AC signal with a range of frequencies to the electrodes using microprobes. The sample was immersed 3 mm deep into the solution during each experiment. It was then rinsed with DI water followed by blow drying using nitrogen. The samples were imaged using a Hitachi S4700 field-emission scanning electron microscope under 1 kV of primary beam acceleration voltage.

In order to be able to explain the experimental results, 2-dimensional (2D) finite element simulations were performed at



**Fig. 1.** Scanning electron micrographs of structures fabricated at various frequencies using solutions with no surfactant and 1 wt% surfactant with 2.5  $\mu\text{g}/\text{ml}$  of CNTs in water. The gap between the electrodes is 4  $\mu\text{m}$ .



**Fig. 2.** Scanning electron micrographs of structures fabricated at various frequencies using solutions with no surfactant and 1 wt% surfactant with 50 µg/ml of CNTs in water. The gap between the electrodes is 4 µm.

the same frequencies as in the experiments using COMSOL Multiphysics [20]. The direction and magnitude of the solution flow, as well as the DEP force, were calculated in each case. Voltages of  $\pm V/2$ ,  $V$  being the applied potential in the experiment, were ap-

plied to the two electrodes in the simulations. The back gate underneath the 2-µm-thick silicon dioxide layer was grounded. Phasor-based quasi static Maxwell's equations were solved to find the electric potential and field distributions in the solution, which was represented by a  $200 \times 150$ -µm region over the electrodes. The electric field distribution was used to calculate the DEP force using

$$\langle \vec{F}_{\text{DEP}} \rangle = \frac{\pi abc}{3} \epsilon_m \text{Re}\{f_{\text{CM}}\} \nabla |\vec{E}|^2$$

and

$$f_{\text{CM}} = \frac{\epsilon_p^* - \epsilon_m^*}{\epsilon_m^*}$$

where  $a$ ,  $b$  and  $c$  denote half of the lengths of the major ellipsoid axes that the nanotube is represented by,  $f_{\text{CM}}$  is the Clausius–Mossotti (CM) factor, and  $\epsilon_p^*$  and  $\epsilon_m^*$  are the particle (in this case the CNT) and medium's complex permittivities, respectively. Also, we have

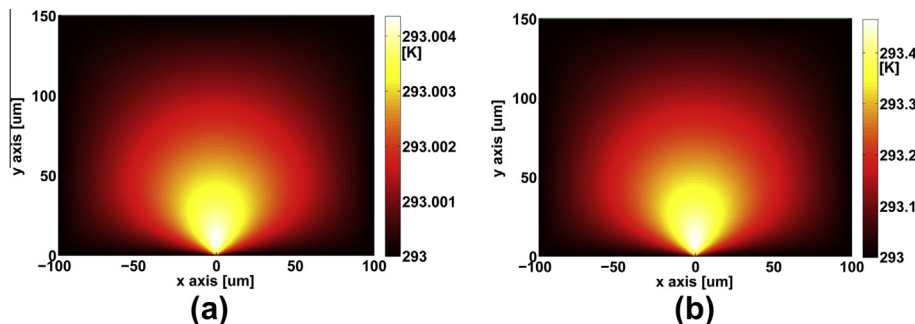
$$\epsilon^* = \epsilon - j \frac{\sigma}{\omega},$$

in which  $\epsilon$  is the permittivity,  $\sigma$  is the conductivity and  $\omega$  is the angular frequency. The CM factor is the frequency dependent part of the DEP force formula. At lower frequencies, the real part of the CM factor depends mostly on the conductivities of the particle and the solution, but in the higher limit the permittivities play the main roles. The border between these higher and lower limits is determined by the relative values of the conductivity and permittivity of the solution and the particle. The DEP force was calculated for metallic CNTs with a length of 1 µm and a radius of 1 nm.

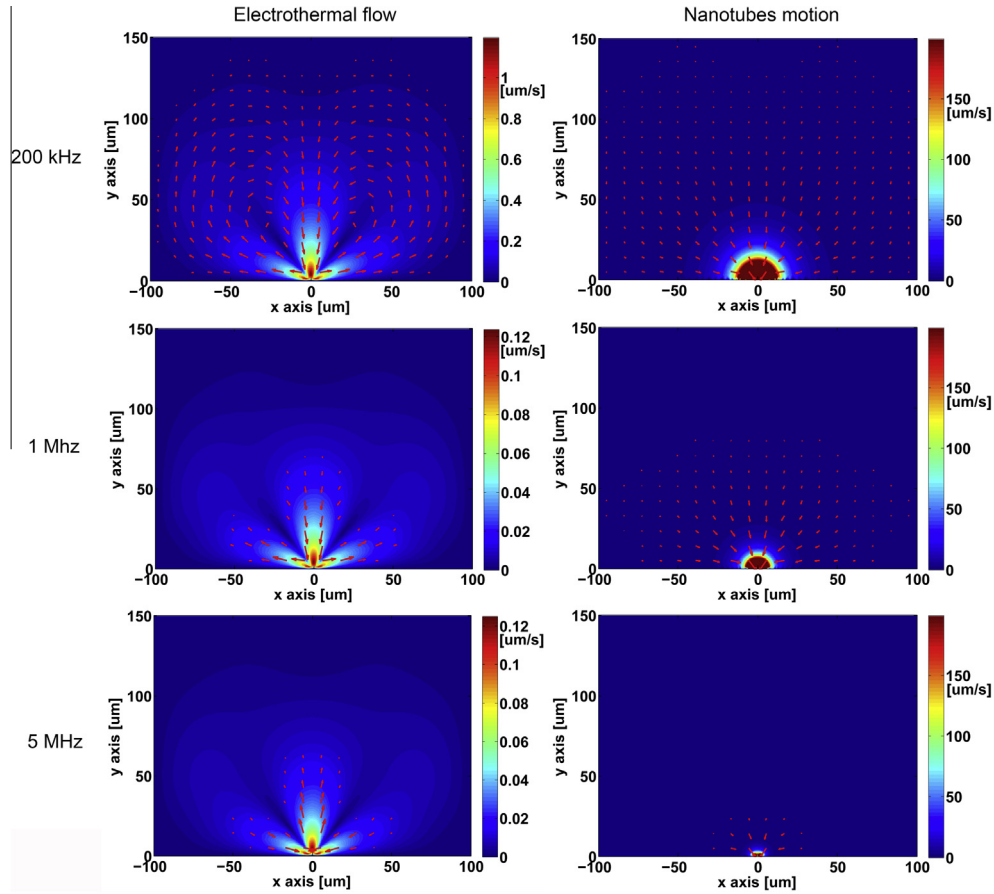
The heat generated in the solution due to the passage of electric current was used in the energy balance equation to find the temperature profile. The temperature gradient and the electric field distribution were then used to find the electrothermal force. Navier–Stokes equations combined with the mass conservation equation were then employed in order to calculate the velocity distribution of the movement of the solution and investigate the resulting patterns.

Electroosmosis is another force that can affect the solution movement in the presence of an electric field. It has been shown that this force is not negligible in the lower frequency range, where the electric double layer can be formed [15,17]. However, for the frequencies typically used in CNT deposition, electroosmosis can be neglected.

The CNTs move with the same velocity as the solution wherever the DEP force is negligible. The change in the velocity of the CNTs as a result of the applied DEP force depends on the friction factor of the CNTs in the solution. For a randomly moving rod-shaped particle, the friction factor is calculated using



**Fig. 3.** Side view of the calculated temperature profile in the (a) no-surfactant, and (b) 1-wt%-surfactant solutions. The two electrodes are located at  $-100$  to  $-2$  µm and  $2$ – $100$  µm on the  $x$  axis. Note that the maximum temperature difference between the hot and cold areas is approximately 100 times higher in case (b).



**Fig. 4.** Electrothermal flow and movement of the nanotubes in the solution caused by electrothermal flow and DEP forces at different frequencies for the no-surfactant solution. The vectors are logarithmically related with the velocity at each point.

$$f = \frac{3\pi\eta l}{\ln(l/r)},$$

in which  $f$  is the friction factor,  $\eta$  is the dynamic viscosity of the solution, and  $l$  and  $r$  are the length and radius of the particle, respectively. The overall speed of the CNTs is determined by

$$\vec{u}_{\text{CNT}} = \vec{u} + \frac{\vec{F}_{\text{DEP}}}{f},$$

where  $\vec{u}$  is the velocity of the solution,  $\vec{u}_{\text{CNT}}$  is the velocity of the nanotubes and  $\vec{F}_{\text{DEP}}$  is the DEP force. More detail about the simulation methodology can be found elsewhere [18].

### 3. Results and discussion

DEP experiments were performed at 200 kHz, 500 kHz, 1 MHz, 5 MHz, and 10 MHz. We observe that not only does the frequency of the applied voltage affect the results, but also the trends are different for the two solutions. Fig. 1 shows the outcome of DEP experiments using solutions with a concentration of 2.5  $\mu\text{g}/\text{ml}$  of CNTs and a deposition time of 30 s. For the no-surfactant case, at lower frequencies most of the nanotubes bridge the electrodes. Increasing the frequency from 200 kHz to 1 MHz directly increases the number of deposited nanotubes. For higher frequencies, the pattern of nanotube deposition changes considerably. The number of deposited nanotubes decreases and, instead of long nanotubes bridging the gap, mostly shorter CNTs deposit along the edges of the electrodes.

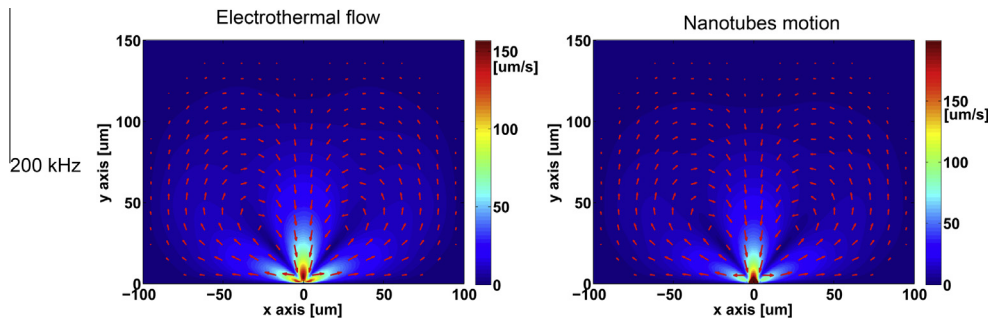
For the solution with 1 wt% surfactant, the CNTs deposit near the electrode edges for all frequencies. Although there seems to

be a slight increase in the number of deposited nanotubes as the frequency increases, this trend is weaker than in the no-surfactant case. As will be seen later, the thermal effects are the root cause of this lack of clear trends with frequency in this range.

Fig. 2 shows the results of DEP experiments using the 50- $\mu\text{g}/\text{ml}$  solution and narrow electrodes. The voltage was applied for 30 s in each experiment. Although the number of deposited nanotubes is much higher compared to the previous case because of the higher CNT concentration, the behavior at different frequencies follows the same pattern. For the no-surfactant solution, at low frequencies the gap between the electrodes is completely filled with CNTs. The area covered by nanotubes increases as the frequency increases from 200 kHz to 1 MHz. At 5 MHz, the number of deposited nanotubes experiences a drastic drop, and increasing the frequency to 10 MHz further decreases this number to just a few. In the 1-wt% surfactant case, CNTs deposit mostly around the edges of the electrodes. There is no direct relationship between the number of nanotubes and the frequency, and the results appear to be somewhat random.

We now turn to the simulation results in order to gain a better understanding of the effective parameters and the forces at work. In the simulations, as expected, the amount of heat generated by the passage of current through the solution was not affected by the frequency in any substantial way and, therefore, the resulting temperature profile was similar at different frequencies. Fig. 3 shows these profiles for the no-surfactant and 1-wt%-surfactant cases.

The gradient of the temperature profile is very high in the case of the 1-wt%-solution, especially near the edges of the electrodes. The electrothermal force directly depends on the temperature



**Fig. 5.** Electrothermal flow and movement of the nanotubes in the solution with 1 wt% surfactant. The results at other frequencies are similar. The vectors are logarithmically related with the velocity at each point.

gradient; therefore, this leads to much higher electrothermal forces in this case compared to when no surfactant is present. Fig. 4 depicts the electrothermal flow pattern in the solution with no surfactants, as well as the movement of the nanotubes as a result of both electrothermal flow and DEP forces acting on them, for three of the simulated frequencies. The maximum velocity on the color coded figures of nanotube movement is set to 200  $\mu\text{m/s}$  in order to bring out the details.

For the no-surfactant solution, the electrothermal force not only weakens at higher frequencies, but also changes direction. For frequencies up to 1 MHz, the electrothermal force assists the overall deposition process by driving the CNTs toward the gap between the two electrodes. On the other hand, in the close vicinity of the gap, the DEP force is dominant. For frequencies higher than 5 MHz, electrothermal flow actually repels the nanotubes from the gap. On the other hand, the DEP force gradually loses its domain of effectiveness and is increasingly restricted to near the edges of the electrodes. This is due to the decrease in the magnitude of the real part of the CM factor for the case of the no-surfactant solution as the frequency increases. The initial increase in the number of deposited nanotubes with increase in frequency (from 200 kHz to 1 MHz) is probably due to the better alignment of the CNTs with the field and, therefore, the higher effect of the DEP force as the frequency increases [21,22].

When a solution containing surfactants is used, the electrothermal force plays a much more pronounced role. In this case, the CM factor does not change in the range of frequencies used here, which means that the DEP force should not change with frequency as much as in the previous case; the simulations also do not show any significant changes in the DEP and electrothermal forces for different frequencies. Fig. 5 shows the electrothermal flow as well as the overall movement of the nanotubes because of both solution movement and the DEP force in this case.

As a final note, the randomness in the deposition patterns caused by thermal agitations seems to be aggravated when a solution with a higher concentration of CNTs is used (see the right-hand side panel of Fig. 2). We believe this is due to the fact that, when a nanotube is deposited, it affects the electric field gradient in its surroundings significantly. This could result in a substantial change in the magnitude and direction of the DEP force acting on other, nearby nanotubes. Added to the thermal movements, this leads to inconsistent and pseudo-random results.

#### 4. Summary

The change in the frequency of the applied voltage during DEP experiments affects the outcome differently for different nanotube solutions. For solutions with low conductivity, the change in the frequency affects the electrothermal flow direction and magnitude

significantly and, more importantly, as the frequency increases, the DEP force becomes more concentrated in the immediate vicinity of the edges of the electrodes. This results in a sudden decrease in the number of nanotubes which bridge the gap between the electrodes at higher frequencies. On the other hand, in the range of frequencies used in practice, changing the frequency does not affect the movement of the solution or the DEP force for solutions with high conductivities. The electrothermal force induces high-velocity movements in the body of the solution and creates a passage for the solution above the gap toward it. In the close proximity of the gap, the DEP force attracts the nanotubes and the electrothermal force drives them toward the edges, which makes the nanotubes deposit on the edges rather than bridge the electrodes. This report represents a step toward engineering the deposition of nanotubes with the DEP method by using the solution conductivity and applied signal frequency more effectively.

#### Acknowledgments

We thank the Natural Sciences and Engineering Research Council, the BCFRST Foundation/British Columbia Innovation Council, the Canada Foundation for Innovation and the British Columbia Knowledge Development Fund for financial support.

#### References

- [1] S. Banerjee, B.E. White, L. Huang, B.J. Rego, S. O'Brian, I.P. Herman, *J. Vac. Sci. Technol. B* 24 (2006) 3173.
- [2] P. Stokes, S.I. Khondaker, *Appl. Phys. Lett.* 96 (2010) 083110.
- [3] A. Vijayaraghavan, S. Blatt, D. Weissenberger, M. Oron-Carl, F. Hennrich, D. Gerthsen, H. Hahn, R. Krupke, *Nano Lett.* 7 (2007) 1556.
- [4] R. Krupke, S. Linden, M. Rapp, F. Hennrich, *Adv. Mater.* 18 (2006) 1468.
- [5] H. Seo, C. Han, D. Choi, K. Kim, Y. Lee, *Microelectron. Eng.* 81 (2005) 83.
- [6] A. Arun, P. Salet, A.M. Ionescu, *J. Electron. Mater.* 88 (2009) 742.
- [7] D. Xu, A. Subaramanian, L. Dong, B.J. Nelson, *IEEE Trans. Nanotechnol.* 8 (2009) 449.
- [8] M. Duchamp, K. Lee, B. Dwir, J.W. Seo, E. Kapon, L. Forro, A. Margez, *ACS Nano* 4 (2010) 279.
- [9] N. Peng, Q. Zhang, J. Li, N. Liu, *J. Appl. Phys.* 100 (2006) 024309.
- [10] S. Shekhar, P. Stokes, S.I. Khondaker, *ACS Nano* 5 (2011) 1739.
- [11] A.J. Blanch, C.E. Lenehan, J.S. Quinton, *J. Phys. Chem. B* 114 (2010) 9805.
- [12] B.I. Kharisov, O.V. Kharisova, H.L. Gutierrez, U.O. Mendez, *Ind. Eng. Chem. Res.* 48 (2009) 572.
- [13] A. Ramos, H. Morgan, N.G. Green, A. Castellanos, *J. Phys. D: Appl. Phys.* 31 (1998) 2338.
- [14] N.G. Green, A. Ramos, A. Gonzalez, A. Castellanos, H. Morgan, *J. Electrostat.* 53 (2001) 71.
- [15] A. Castellanos, A. Ramos, A. Gonzalez, N.G. Green, H. Morgan, *J. Phys. D: Appl. Phys.* 36 (2003) 2584.
- [16] Y. Lin, J. Shiomi, S. Maruyama, G. Amberg, *Phys. Rev. B* 76 (2007) 045419.
- [17] B.R. Burg, V. Bianco, J. Schneider, D. Poulikakos, *J. Appl. Phys.* 107 (2010) 124308.
- [18] A. Kashefian Naieni, A. Nojeh, *Nanotechnology* 23 (2012) 495606.
- [19] <http://www.nano-lab.com>.
- [20] <http://www.comsol.com>.
- [21] M. Dimaki, R. Boggild, *Nanotechnology* 16 (2005) 759.
- [22] X.Q. Chen, T. Saito, H. Yamada, K. Matsushige, *Appl. Phys. Lett.* 78 (2001) 3714.