THE APPLICATION OF DIELECTROPHORESIS TO NANOWIRE SORTING AND ASSEMBLY FOR SENSORS

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***Abstract*–This manuscript describes a stochastic process in which a collection of nanowires is assembled on an array of electrodes for the purpose of making miniature gas sensors. The wires are not individually placed on the electrodes, but are assembled using fields, including fluid, gravity, and dielectrophoretic forces. Assembly through fields is scalable to high-throughput manufacturing processes, although it is also an underactuated control problem. To design an economical manufacturing process, a predictive physical model must first be developed. This model can then be used to design processes and devices that are less sensitive to the inherent noise in the assembly process, or that even provide built-in feedback during assembly. Real time feedback control could also be implemented using impedance spectroscopy. This work reviews the past research in nanowire assembly and describes some preliminary work of our group in the assembly tin oxide nanowires for gas sensors.**

I. INTRODUCTION

In recent years nanoscientists have generated fascinating new materials with previously unattainable properties. For several of these nanostructured materials it should be possible to take advantage of readily accessible field induced manipulation of materials. However, integrating these materials into nanometer-scale devices that impact our everyday lives has not yet followed, in part due to the difficulty in producing such materials in the repeatable manner necessary for manufacturing. Applications including nanowire-based electronics, nanosensors, optical systems, flat panel displays that use carbon nanotubes, high heat flux modified surfaces and biological and biomedical applications are on the forefront. However, for all of these to be realized there is a fundamental requirement for the controlled assembly of the nanowires to the substrate or surface.

Manipulation of particles and in particular biological cells, viruses and proteins has been reported utilizing dielectrophoresis and a comprehensive review is given by Burke [1]. Dielectrophoresis was pioneered with the early work of Pohl in the 1950's. His book [2] and the text by Pethig on biological application [3] provide the foundation for this field. More recent text by Jones [4] focuses on particles, and the application of dielectrophoresis to manipulation and sorting of bioparticles is reviewed by Huang *et al.* [5].

A. Principle of Dielectrophoresis

Dielectrophoresis (DEP) is defined as the polarization and associated motion induced due to the effect of an inhomogeneous electric field. The induced motion is determined by the dielectric properties of the nanowire or particle, unlike electrophoresis where motion of the particle or nanowire is determined by the magnitude and polarity of the net electrical charge. The advantage for biological particles of using DEP over electrophoresis, which relies on the electrophoretic mobilities of particles, is the fact that most have similar electrophoretic mobilities and hence it becomes very difficult to distinguish between them. With DEP, electrophoretic mobilities do not come into play and it is easier to separate two different particles from a solution. Both alternating current (AC) and/or direct current (DC) electric fields may be employed. Also the DEP effect is independent of the charge on a nanowire, so that neutral nanowire can be subject to this effect, making it more versatile in its application to nanowire separation and assembly. There are two different effects associated with DEP: positive and negative DEP. Positive DEP occurs when the nanowire is more polarizable than the medium, causing the wire to be attracted to maxima of the electric field intensity. The reverse is true for negative DEP.

B. Dipole Approximations

Depending upon the orientation of the wire, there will be resultant torque aligning the nanowire to the field lines, and a force which will produce translation of the nanowire, as shown in Figure 1. The *dielectrophoretic approximation* is often used to compute the force and torque, by assuming that the electrode dimensions and hence the scale of the electric field gradient in space is much larger than the nanowire dimensions. When these assumptions are made, the following expressions represent the force and torque on a particle or wire:

$$F_{dipole} = p \cdot \nabla E$$
$$T_{dipole} = p \times \nabla E \qquad (1)$$

where p is the dipole moment of the wire, and ∇E is the gradient of electric field.

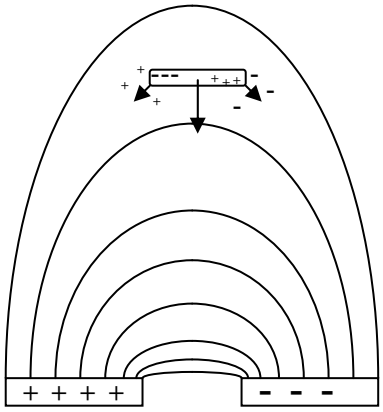

Fig. 1 Electric field distribution between electrodes.

For a nanoparticle or nanowire of volume V, suspended in a medium of absolute permittivity ε_m, the dipole moment p is computed using the *effective moment approximation* [4]. The field induced by the external electric field is equivalent to field generated by a dipole. For a spherical body, the resulting expression is

$$p = 3V\varepsilon_m K(\omega)E$$

$$F_{DEP} = \frac{3V}{2}\varepsilon_m \mathrm{Re}\left(K(\omega)\right)\nabla\left(E\right)^2 \qquad (2)$$

where F_{DEP} is the time-averaged force, ω is the AC frequency, and Re*(K(ω))* is the real part of the Clausius-Mossotti (CM) factor which can be defined using equation, as follows for a lossy dielectric media:

$$K(\omega) = (\varepsilon_p^* - \varepsilon_m^*)/(\varepsilon_p^* + 2\,\varepsilon_m^*) \qquad (3)$$

where ε_p^* and ε_m^* are the relative complex permittivities of the nanowire and medium respectively. The complex permittivity is defined as $\varepsilon^* = \varepsilon - j\,\sigma/\omega$, where σ is the conductivity. For nonspherical bodies, analogous formulas have been derived [4, 7], but they are also still subject to the dielectrophoretic approximation.

If a nanowire has a surface coating or surface conductivity this can also contribute to the imaginary part of the dielectric constant. The following substitution has been utilized for particles and by [4,6] to estimate forces on nanoparticles.

$$\sigma_p = \sigma_b + \frac{2K_s}{r_e} \qquad (4)$$

where r_e is the particle effective radius and K_s is the surface conductivity. The value of the CM factor, which can be calculated from the properties of the medium and the nanowire, may be positive or negative. If this value is negative then a negative DEP will occur, while a positive CM factor is indicative of positive DEP.

C. Limitations of the Approximations

In addition to the geometrical constraints of the dielectrophoretic approximation, an assumption is made on the time response of the system. The average DEP force given in equation (1) is derived by assuming that the induced dipole switches instantaneously, in-phase with the externally applied electric field for a dielectric particle. For a conductive particle a phase difference can results based upon the carrier relaxation with in the material. In fact, this is the fundamental mechanism which allows the separation of carbon nanotubes of differing electrical conductivity to be carried out [26]. Taking only the real part of the CM factor uses the effective moment method which is mathematically easier to construct than a full tensor analysis using Maxwell's Equations [8], but may not accurately reflect the physics.

D. Effect of Electrode Geometry on Field Gradient

As can be seen from equation (2) the electric field distribution is a critical parameter in DEP based devices and needs detailed study. At the boundary between the electrode and the fluid the field is perpendicular to the surface. Hence the higher field is established at the smaller radius, for example for a cylindrical electrode:

$$E = \frac{V}{\ln(4h/d)}\frac{1}{r} \qquad (5)$$

where d is the diameter of the electrode, h is the distance from the electrode to a second planar electrode, and r is the radial distance from the electrode center [32]. A number of electrode geometries have been tested including sawtooth, castellated, interdigitated, spiral, chevron and quadrupole [1]. Carbon nanotubes have even been used as electrodes to minimize the electrode diameter and thus maximize the DEP force [32]. The quadrupole electrode provides a local maximum field gradient that can be utilized to trap a particle without contact to the electrode surface [9]. So-called particle traps are able to locate a biological particle for subsequent analysis for example.

E. Nanowire Dynamics

The polarized nanowires will move in response to the applied electric field and field gradient so one must also consider the Coulomb force, forces of gravity (through buoyancy), and viscous drag.

$$F_{Total} = F_{Coulomb} + F_{DEP} + F_{Boyancy} + F_{Drag} + F_{Brownian}$$

Brownian motion may also play a role for smaller volume nanowires where the energy in the system is comparable to the thermal energy kT and produce a random walk motion.

II. Modeling of DEP Effect

The DEP forces on an object are generated by gradients in the electric field. Much of the work in modeling DEP forces has focused on computing the electric field, with the assumption that the object does not perturb the externally applied field. Interdigitated electrode arrays (IDA) are a frequently selected method for producing high electric field gradients, and as the electrode spacing is reduced the field is proportional to the inverse of the gap. Modeling of the field distribution in this simple geometry has been solved analytically with the Schwartz-Christoffel transformation [10]. Others have used finite element analysis to determine field distribution, because the effect of polarizable material in the fluid can also be included and because more complex electrode geometry can be considered [11,12].

The DEP forces on an object can be calculated by directly integrating the charge and electrical field over the object, or can be approximated with simpler equations using the dielectrophoretic approximation and the effective moment method described in the previous section. It is important to note that these approximations are derived by assuming that the electric field changes only slightly across the objects. While this approximation is reasonable for a small particle, it clearly is not justified in our application, since the nanowire length (10-20 μm) is similar to the electrode spacing (20 μm).

In a previous study on E-coli particles we used a simple 2D model and electrostatic solvers in ANSYS to compute the electric field gradient [13] Using a similar approach, Albrecht *et al.* [14] has made a useful model for a design optimization of collection of biological cells in a non conductive medium. Although simple force expressions (such as equation (2)) are useful for scientific investigation, we expect that the numerical approach will be needed for process and device design so that realistic geometries and conditions can be quantitatively described.

III. Prior Work on the Separation and Assembly of Nanowires and Nanotubes

One of the earliest reports on the purification and alignment of carbon nanotubes with AC DEP in isopropyl alcohol as given by Yamamoto *et al.* [15] at aluminum electrodes with 400 μm gaps. The longer nanotubes were observed to have the greater degree of orientation at high frequency 10 MHz (compared to 10Hz), with an estimated field of 2.2 kV/cm. Assembly of carbon nanotubes and nanowires has been demonstrated by several groups [16-18]. The rapid assembly of metallic nanowires demonstrated by Smith *et al.* [19] in isopropyl alcohol with field strengths estimated to be in the range 10 – 140 kV/cm for a 30V (RMS) sine wave at frequency of 1 kHz produced alignment in approximately 5-9 seconds. Directed placement of carbon nanotubes has also been demonstrated in an aqueous buffer at electron beam defined 10-80 nm electrode gaps using 5 MHz, AC bias 0.5-2.5 V and provided selective deposition of the carbon nanotubes without carbon nanoparticles [20]. A pronounced effect of the electrode material has also been observed by Krupke *et al.* [21] for nanotubes suspended in DMF with DEP fields between 1 kHz and 10 MHz. Here the high frequency produced alignment of single nanotubes rather than bundles of nanotubes. While gold produced bundles of nanotubes and the silver electrodes tended to interact more strongly with the carboxyl functionalized carbon nanotubes surface so that very few bundles or single tubes were collected.

Alignment with dc fields only was demonstrated by Kumar *et al.,* [22] and attraction to the anode suggests a negative charge on the carbon nanotube. More dispersed and controlled alignment was observed for DMF compared to ethanol solvent, and the alignment observed at electric fields between 25 kV/cm and 100 kV/cm.

Alignment is generally improved in a mixed AC and DC field. Single walled carbon nanotubes were collected by Chen *et al.* [23] at gold IDA electrode the tubes were highly aligned in the direction of the electric fields (magnitude 50 kV/cm). Chung and Lee [24] demonstrated assembly of a single carbon nanotube at 20 nm gap electrodes. The electrode tip radius had a strong influence on the assembly and alignment of the nanotubes. The nanotubes were observed to respond slowly to DC fields compared to carbon particles present in the sample. However, the nanotubes were attracted at 5 MHz AC field compared to the carbon particles. Typical field intensity utilized were the order of 5 kV/cm at 10 MHz. Estimate of the field gradient as a function of tip radius were made with FEMLAB and how the amount of DC and AC field could influenced the number of tubes attached to each electrode [25]. However, although the field produced was higher for small radii, if the electrodes were too sharp then it was difficult to achieve a directional deposition. Examination of how close electrodes could be located relative to one another indicated a gap of at least two times the electrode width should avoid interference.

Separation and enrichment of metallic and semiconducting carbon nanotubes has demonstrated shown by Chen *et al.* [26]. Separation of the metallic from the semiconducting nanotubes was achieved in a liquid droplet on chip. A greater degree of separation was demonstrated by Lee *et al.* [27] with the metallic tubes removed from the sample to a degree that after 7 cycles an enrichment of 95% was achieved. The positive DEP force on the metallic nanowires brought them to a position between the electrodes leaving the stock solution enriched with semiconducting nanowires.

Assembly at individual nanometer scale electrodes has been demonstrated by Jin *et al*. [28] for the organization of nanowires to build electronic devices. The nanowires were obtained with a distribution of lengths and suspended in ethanol before introduction to the chip with pre-defined gold electrodes. Electron beam lithography was used to pattern electrode array at 300 nm gaps between the fingers. Once capture of a wire had been achieved the local field was reduced and reduced the probability of assembly of a second nanowire. This limit of control of probability of the assembly produced an array of nanowires with good success, about 90% of the electrodes were occupied with nanowires.

Dielectrophoretic manipulation of viral particles 18 nm diameter and 280 nm in length was effective with high frequency ac field at 5-50 MHz [29]. In this study saw-tooth gold electrodes were used to provide a high field gradient at the tips. The orientation depended upon the polarization of the viral particles and alignment was possible either parallel or perpendicular to the field. In addition, by sweeping over the frequency a DEP force cross-over point was determined and through fitting with simple model an estimate of the conductivity for the viral particle was determined.

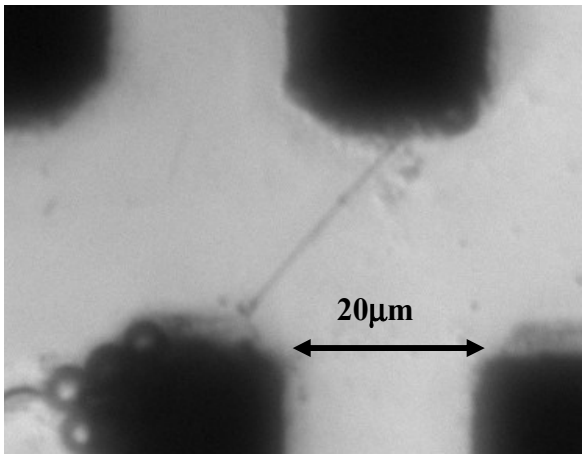

Fig. 2: Nanobelt attracted between castellated gold electrodes. The SnO_2 nanobelts were suspended in ethanol.

IV. Our Preliminary Results

Dielectrophoresis was used to electrically manipulate semiconducting oxide nanobelts (SnO_2) that were synthesized with a high temperature process [30]. The nanobelts used in the tests had a width of around 200 nm, and AFM measurements indicate they are 30-40 nm thick. Figure 2 shows the DEP electrodes as observed under the optical microscope. The electric field is between the castellated aluminum electrodes with a minimum gap of 20 μm. The SnO_2 nanobelt suspension was introduced in the microchannel and manipulated using 9.8 V AC peak-to peak with different frequencies. In the 10 Hz-1 kHz frequency range repulsion of the nanobelt occurred, while in the 1-10 MHz frequency range attraction of the nanobelts between the electrodes was observed. Once the nanobelts touched the electrodes, it remained stuck there. The dielectrophoretic effect was lost, since the nanobelts were bridging the gap, providing a built-in feedback for the assembly process. More effective detection and control might be achieved with a more resistive film such that the local potential could then be a function of the nanowire attachment such that at locations occupied by nanotubes the field can be reduced significantly. When a DC voltage was applied between the electrodes, a current flow was observed. I-V characteristics were recorded for these wires and found to be a function of exposure to gases at room temperature. In particular, this device demonstrated sensitivity to 2 ppm ammonia indicating potentially for used as a gas sensor [31].

We have also performed calculations of the electric field for a tin oxide nanowire in ethanol. The relative permittivity used for the ethanol is 25, and the permittivity for the tin oxide wire is $12–j50{,}000/(2\pi 1000)/\varepsilon_0$, to represent a typical AC frequency of 1000 Hz (ε_0 is the permittivity of free space). A typical calculation is shown in Figure 3.

Simple models based on the dipole approximation fail to capture the transition from repulsive to attractive behavior. At low frequency, the dipole model predicts that the conductivity of the wire and medium to dominate the DEP force, creating a strong attraction of the wires to the electrodes. At the higher frequencies, weaker attraction is predicted by the dipole model since the dielectric constant of the wire is lower than that of the ethanol. Clearly, this simple model does not account for all the observations.

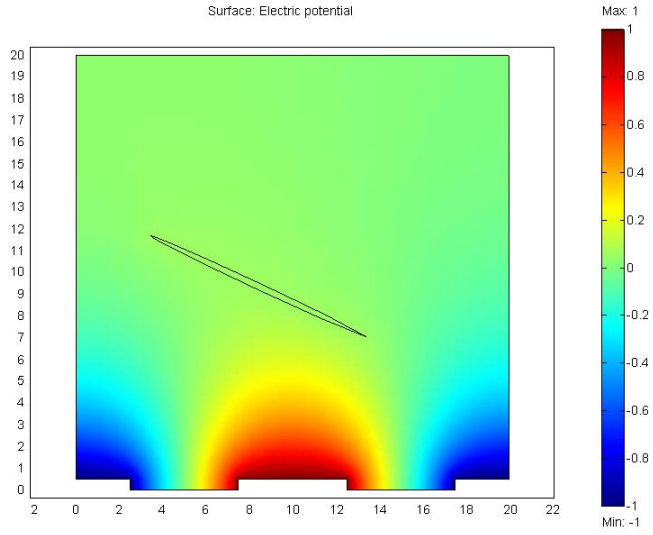

Fig. 3: Potential distribution in 2-D simulation above interdigitated electrode array with nanowire of comparable dimensions to the electrode spacing. The calculation was performed using FEMLAB.

Further characterization of material properties of the nanowires is needed, since the properties may not match those of bulk tin oxide. Surface charge, on the nanowires or the glass substrate, may also be altering the system behavior. Moreover, the dipole approximation is clearly not valid since the wires are long relative to the electrode spacing. Ongoing work in developing a predictive model of this assembly process will enable the design of an optimized process, and analysis of feedback controllers to reduce process variation.

V. Discussion and Conclusions

Several groups have demonstrated the manipulation and assembly of metallic nanowires and carbon nanotubes at microelectrodes utilizing DEP. The selective transport of the nanowires to the electrode surface is a function of their dielectric properties. However the dispersion and forces generated are based upon incorrect assumptions. This is due to their use of the dipole approximation which assumes the object dimensions are much smaller than the field gradient, which is certainly valid for nanoparticles, but invalid for nanowire. To develop predictive models that can be used for process design and process control, development of models based upon appropriate manipulation of Maxwell's equations is required, which would also find utility in accurate DEP studies of particles. The assembly of nano*particles* using DEP is challenging due to Brownian motion, but controlled assembly of nano*wires* appears to have merit as there is a significantly larger force compared to what one would expect from a particle of equivalent volume [29]. However, the greater challenge is to do so in a reproducible manner and holds great promise for directed assembly because translation, alignment, rotation and levitation are all possible under the right conditions.

VI. Acknowledgments

Financial support was provided by the Georgia Nanoscience/ Nanoengineering Research Program. In addition, the financial support of Nanoscience and Nanotechnology Fellowship Committee of Georgia Institute of Technology is gratefully acknowledged.

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