OPTIMIZING DIELECTROPHORETIC ASSEMBLY FOR
CARBON NANOTUBE-BASED NEMS DEVICES

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ABSTRACT

Though graphene and bio-molecules have attracted intense interest as the building elements for future nanodevices, the design and construction of carbon nanotube (CNT) nanoelectromechanical systems (NEMS) continue to progress rapidly. Lithography-based techniques often have drawbacks of low-throughput, high-cost, long-operating time and low-reproducibility. Because of compatibility with the standard microfabrication techniques, dielectrophoresis (DEP), in particular, provides an efficient and inexpensive tool for parallel fabrication of high quality carbon nanotube nanodevices. These devices have been reported as good candidates for many applications, such as mass sensors in femto-gram ranges, force sensors at pico-Newton scales, and resonators at GHz ranges.

Control over DEP process parameters including the initial conditions of suspensions, the induced electric fields etc., is crucial for large-scale assembly of sophisticated nanostructures. Based on a theoretical analysis and finite element model, the assembly behavior of CNTs is investigated in this thesis. Several optimizing approaches are proposed to realize DEP assembly of CNT-based NEMS devices for mass-production with high-precision. It is demonstrated that by designing the electrode configuration, controlled positioning and alignment of nanotubes can be achieved. In order to assemble cantilever CNTs on protruding electrodes, a floating-electrode DEP method that eliminates the irresolute deposition of nanotube on the electrode tip has been developed with attributes to facilitate four-terminal electrical measurement.

Apart from tuning the intrinsic parameters of DEP process, a thermal field is integrated with the non-uniform electric field. The induced thermophoresis opens up new perspective on mediated DEP assembly with the advancement of improved assembly range and speed. Optimizing techniques for DEP assembly enhance the assembly yield and efficiency and offer great potential in developing self-assembly methods for next-generation NEMS devices, enhancing a possibility of their practical manufacturability and commercialization.
ZUSAMMENFASSUNG


# TABLE OF CONTENTS

ACKNOWLEDGEMENT .............................................................................................................. I
ABSTRACT ................................................................................................................................. III
ZUSAMMENFASSUNG ............................................................................................................... IV
TABLE OF CONTENTS .............................................................................................................. VI

1 INTRODUCTION ................................................................................................................... 1

1.1 STATE-OF-THE-ART FOR DEP ASSEMBLY ................................................................. 1
1.2 MEDIATED DEP ASSEMBLY WITH EXTERNAL ASSISTANCE ............................... 4
  1.2.1 Magnetic field-assisted DEP ................................................................................. 4
  1.2.2 Fluid field-assisted DEP ..................................................................................... 5
1.3 RESEARCH ON DEP ASSEMBLY OF CNTS ............................................................... 7
1.4 THESIS MOTIVATION ................................................................................................. 7
1.5 THESIS ORGANIZATION ............................................................................................ 9

2 THEORY AND MODELING OF DIELECTROPHORESIS .................................................... 11

2.1 DEP THEORY .................................................................................................................. 12
  2.1.1 DEP Force and Torque ....................................................................................... 13
  2.1.2 Electrohydrodynamics of CNT Assembly ............................................................ 15
2.2 DEP MODEL ..................................................................................................................... 16
2.3 PROCESS PARAMETERS FOR DEP ASSEMBLY ......................................................... 20
  2.3.1 CNT Suspension ................................................................................................. 20
  2.3.2 Dielectric Properties of the System .................................................................... 21
  2.3.3 Non-uniform Electric Field ................................................................................. 22
  2.3.4 Electrode Configuration ...................................................................................... 23
2.4 SUMMARY ....................................................................................................................... 23

3 SHAPING ELECTRODES FOR CONTROLLED DIELECTROPHORETIC ASSEMBLY ...... 25

3.1 LOCAL SHAPE OF ON-CHIP ELECTRODE PAIR ...................................................... 26
  3.1.1 Results ................................................................................................................. 26
3.2 LOCAL SHAPE OF PROTRUDING ELECTRODE PAIR ............................................. 30
  3.2.1 Standard Operating Procedure ......................................................................... 31
    3.2.1.1 Defining the Protruding Nanoelectrodes ....................................................... 33
    3.2.1.2 Nano-object Assembly onto Protruding Nanoelectrodes ............................ 36
  3.2.2 Results ................................................................................................................. 36
    3.2.2.1 Electrical Measurement .............................................................................. 39
    3.2.3.2 Discussion ....................................................................................................... 40
  3.2.4 Failure Mode Analysis ......................................................................................... 42
3.3 SUMMARY ....................................................................................................................... 43

4 FLOATING-ELECTRODE DIELECTROPHORETIC ASSEMBLY OF MWNTS ONTO  PROTRUDING NANOELECTRODES ....................................................................................... 45

4.1 CONCEPT AND THEORY ............................................................................................. 46
4.2 FLOATING-ELECTRODE DEP APPROACH ................................................................ 48
4.3 DEVICE STRUCTURE AND FABRICATION PROCEDURE ...................................... 50
4.4 RESULTS ....................................................................................................................... 53
  4.4.1 FEM modeling .................................................................................................... 53
# Table of Contents

4.4.2  Floating electrode DEP assembly results .............................................................. 55  
4.4.3  Failure modes analysis ......................................................................................... 58  
4.5  SUMMARY ................................................................................................................. 59  

5  ELECTRICAL CHARACTERIZATION OF MWNTS USING FOUR-TERMINAL MEASUREMENT .............................................................................................................. 60  
5.1  NANOSTRUCTURE FOR FOUR-TERMINAL MEASUREMENT ........................................ 61  
5.2  CONTACT RESISTANCE ............................................................................................. 62  
5.3  CONCEPT OF FOUR-TERMINAL MEASUREMENT ........................................................ 63  
5.4  RESULTS ....................................................................................................................... 64  
5.5  DISCUSSION & ANALYSIS .......................................................................................... 66  
5.6  SUMMARY .................................................................................................................... 67  

6  THERMOPHORESIS ENHANCED DEP ASSEMBLY OF CNTS ......................................... 68  
6.1  CONCEPT .................................................................................................................... 69  
6.2  THERMOPHORESIS OF CARBON NANOTUBE ................................................................ 70  
6.3  THERMOPHORESIS ENHANCED DIELECTROPHORESIS OF CNTS ............................. 73  
6.4  APPLICATION & DISCUSSION .................................................................................... 75  
6.4.1  Temperature Field .................................................................................................... 75  
6.4.2  Thermophoretic Effects ............................................................................................ 78  
6.5  EXPERIMENTAL RESULTS ........................................................................................ 81  
6.6  SUMMARY .................................................................................................................... 85  

7  CONCLUSION AND OUTLOOK ...................................................................................... 86  

REFERENCE ....................................................................................................................... 90
1 INTRODUCTION

High precision assembly and fabrication of microstructure- or nanostructure-based functional devices and systems has led to tremendous advances in nanotechnology applications. The basic structures, e.g., electrode patterns, of such devices can be manufactured by techniques that have been commonly practiced in modern electronics industry, i.e., “top down” lithography-based techniques such as electron-beam lithography [1, 2], focused ion beam [3, 4] and interference lithography [5-7]. However, for devices whose function relies on nanostructured components such as carbon nanotubes or bio-materials [8-12], lithography alone is usually incapable of fulfilling all manufacturing requirements. This is where “bottom up” assembly methods come into play [13-16]. “Bottom up” methods allow for the incorporation of nanostructured components into the basic structures of lithographically generated devices [17-21]. Dielectrophoretic self-assembly is one of the emerging fabrication technologies that could have a profound impact on the massive and commercial manufacturing of microelectromechanical systems (MEMS) and nanoelectromechanical systems (NEMS) [22-24].

1.1 STATE-OF-THE-ART FOR DEP ASSEMBLY

Dielectrophoresis (DEP), which categorizes the movement of polarizable particles induced by a non-homogeneous electric field [25], has been studied for decades. In a uniform electric field (Figure 1.1(a)), Coulomb forces are generated on both sides of a particle which are equal in magnitude and opposite in direction, resulting in zero net force on the particle. However, when the electric field is non-uniform (Figure 1.1(b)), the Coulomb forces on either side of the particle can be different, and the overall force results in particle motion. Since the direction of the force is determined by the spatial variation of the field, the particle always moves toward/against the direction of the electric field maxima. The phenomenon can be observed under the influence of either alternating current (AC) or direct current (DC) electric fields [26].
Compared to many other bottom-up assembly techniques that employ inter-particle forces (such as electrostatic forces [27, 28], van der Waals interactions [29] and surface tension [30]) for spontaneous assembly, DEP overcomes the disadvantages such as the need for complicated setups and poor controllability. Moreover, it is highly versatile since most materials are polarizable with no need for special surface functionalization. Because DEP assembly is usually performed at room-temperature, in a non-corrosive fluidic environment and at low voltage, this electric field-based method is compatible with further post-processing steps such as those used in integrated circuit (IC) manufacturing. DEP can also be scaled to the wafer level, making mass production of nano-devices feasible. It has been proven a fundamental method for manipulating micro- and nano-sized particles in many applications including bio-trapping, bio-separation, optoelectronics, sensors, field-effect transistors, transducers and resonators [26, 31-39], several of which are shown in Figure 1.2.

Although significant progress has been made in assembling nanoscale devices using dielectrophoresis, it has a major drawback related to the relatively low reproducibility. Because dielectrophoretic assembly is fundamentally a stochastic process depending on various parameters such as experimental settings and initial conditions, it is quite challenging to identify and maintain the optimum assembly conditions from batch to batch. Future research and development on DEP assembly
methods should largely lie in improving the assembly yield and precision with high reproducibility before the methods can be used in industrial processes.

**Figure 1.2** (a) Fluorescence image of DNA molecules attached to selected electrodes by DEP trapping. (b) The SEM image of DEP trapped protein structures, which are attracted to the high electric field regions by positive DEP force. (c) ZnO nanowire field-effect transistors fabricated by DEP assembly. (d) Supramolecular switches based on bidirectional linear bearings produced by DEP assembly and shell-engineering. (Images adapted from reference 26, 35, 36)

To address the above mentioned challenges, many efforts have been made to investigate the effects of different process parameters on the performance of DEP assembly. Recent studies have provided some qualitative insights in this regard, which cover the influences of the fluid conductivity, target material concentration, the electric field strength, the AC frequency and the DEP duration time [40-46]. These results contribute to the overall control of the assembled nanostructures (from dense arrays to clean single nano-objects) via adjusting of the process parameters. To achieve better control over the dimension, orientation and morphology of the assembled individual materials, other pertinent factors including the electrode gap distance and the size of electrode patterns have also been investigated [47, 48].
INTRODUCTION

1.2 MEDIATED DEP ASSEMBLY WITH EXTERNAL ASSISTANCE

Conventional dielectrophoresis for assembly has been further developed with the aid of force fields (e.g. magnetic field and fluid field) external to the electric field. Sophisticated device structures and enhanced functionalities, e.g. more flexible control over nano-object movements) can be realized with externally mediated DEP approaches.

1.2.1 MAGNETIC FIELD-ASSISTED DEP

Dielectrophoresis can be implemented under the influence of a magnetic field on a hybrid IC/microfluidic chip [49]. Note that this external magnetic field should be distinguished from the AC electric field induced internal magnetic field. Dielectrophoresis has the function of trapping and positioning living cells inside small volumes of a carrying fluid, while the controlled external magnetic field can be used to move objects tagged with magnetic nanoparticles that have no response to DEP. The combination of both magnetic and electric fields for assembly of micro- and nano-objects [50, 51] onto a single chip further expands the capabilities and generality of the platform, leading to exciting scientific discoveries and technological applications.

One example of magnetic field assisted DEP assembly is shown in Figure 1.3. In panels (a) and (b), the hybrid chip is divided into an array of metal pixels, each of which can be powered with a radio frequency (RF) voltage to locally apply DEP forces. A matrix of conducting wires underneath the DEP pixel arrays are used to generate the external magnetic field. The chip’s capability to control microscopic objects using both DEP and magnetic field has been nicely demonstrated by trapping a vesicle with DEP while attracting the iron oxide nanoparticles contained in the vesicle via the magnetic force. The vesicle is held in place with DEP forces and turns to a thin tether when the iron oxide nanoparticles are pulled towards the magnetic field maximum (Figure 1.3(c)). When the magnetic field is switched off, surface tension in the vesicle membrane pulls the tether back into the original shape (Figure 1.3(d-e)). Such hybrid chips integrating DEP and magnetism effects should enable many experiments to be carried out at the same time, thus serving as a versatile
platform to control microscopic objects for a wide range of biological and chemical applications [52, 53].

![Figure 1.3](image)

**Figure 1.3** (a) Electric field $E$ induced on the DEP pixel. (b) Magnetic field $B$ generated from underneath the magnetic matrix. (c) A vesicle is held in place with a DEP pixel while a tether is pulled by the magnetic force. The yellow square shows the activated DEP pixel, and the red lines show the wires in the magnetic matrix that are switched on. Iron oxide nanoparticles are suspended in the fluid inside the vesicle. From (c) to (e), the magnetic field is turned off and the tether is pulled back to recover the original shape of the vesicle. (Images adapted from reference 49)

**1.2.2 Fluid field-assisted DEP**

One example of the fluid field-assisted dielectrophoresis method is shown here for the assembly of individual silicon carbide (SiC) nanowires with better controlled orientation and enhanced deposition yield [54]. As illustrated in Figure 1.4, this method combines an AC electric field and a shear flow field in a microfluidic channel which contains the SiC nanowire carrying fluid. In this fashion, more SiC nanowires are assembled between the electrode gap than that achieved with random flow deposition [55]. During the assembly, the fluid flow delivers and orients the nanowires in the vicinity of the gap where the nanowires are attracted and deposited by a DEP force. Precise control over the fluid flow and the dielectrophoresis
parameters shows various interesting phenomena such as fixing, shifting and uniform spacing of nanowires during the assembly process.

**Figure 1.4** (a) A schematic diagram of the fluid field-assisted DEP assembly process. The microfluidic channels are filled with ethanol. Video recorded images of SiC nanowires assembled onto the electrodes in the fluidic channels for (b) 5 µm gap electrodes, (c) 15 µm gap electrodes and (d) 50 µm gap electrodes. (Scale bar, 50 µm). (Images adapted from reference 54)

Being carried by a fluid at a controlled flow rate, the SiC nanowires were transported through the microfluidic channel from right to left by capillary action (Figure 1.4(a)). When the AC electric field is imposed on the electrode pairs, DEP force starts to take effect on SiC nanowires. In the case of 5 µm and 15 µm wide gaps, the nanowires were deposited across the electrode gaps (Figure 1.4(b-c)), whereas most of the nanowires tend to be attracted to the edge of the right-hand-side electrode (i.e., the downstream electrode) with a 50 µm gap because of the flow direction (Figure 1.4 (d)). It is also found that most nanowires were deposited between the gap rather than the side areas in that the fluid flow direction in the gap is the same as the electric field direction. The nanowires taking the direction of the fluid flow experience a much smaller drag force than that experienced by those aligned perpendicular to the fluid flow direction.
INTRODUCTION

Similar work has been done by performing fluid field-assisted DEP assembly in a thin channel. By balancing the dielectrophoretic, hydrodynamic and surface forces, it is possible to realize single nanowire assembly over a large number of electrode pairs with high yield and self-limiting properties [38].

1.3 RESEARCH ON DEP ASSEMBLY OF CNTS

Owing to their interesting electrical and mechanical properties, carbon nanotubes (CNTs) are widely explored as highly promising building blocks for future nanosystems [56]. The size of NEMS devices that are defined by lithographic process are now approaching the dimensions of carbon nanotubes, making it an attractive subject for assembly of CNTs onto NEMS structures. However, fabrication of CNT-based devices at low cost and a high throughput remains one of the main scientific barriers to be overcome.

Among numerous efforts that have been made to make CNT-based nano-devices, dielectrophoretic assembly has overcome disadvantages such as the need for complex setups and poor controllability, allowing for substantial control over the assembly precision and alignment of nanotubes. Because of the compatibility with post-processing steps in consumer electronic applications, dielectrophoretic assembly has drawn considerable interests from the scientific community during the past decade. Reported achievements in manipulation CNTs using dielectrophoresis are exemplified by the separation of metallic CNTs from semiconducting CNTs [57], high resolution atomic force microscopy (AFM) tips [58] and nanoelectronic devices [59, 60].

1.4 THESIS MOTIVATION

Motivated by the vast applications of CNT-based nanostructures, this thesis presents a hybrid nanofabrication approach that synergistically integrates bottom-up and top-down unit processes to assemble CNTs onto nanoelectrodes for creating complex nanostructures. The goal is to achieve CNT assembly with high spatial precision and with efficiencies in scale and cost reduction. Here, the dielectrophoretic assembly technique is the central tool, which in certain cases will be aided by external fields, to integrate CNTs onto lithographically defined nanoelectrode patterns on silicon chips.
A universal finite element model is constructed to understand the physics of DEP assembly process and simulate the behavior of CNTs in a fluid being subjected to a non-uniform electrical field, fluid drag forces and thermal forces. This model gives insights into the contributions from both internal factors (e.g. the electrode shape and configuration) and external factors (such as the thermal field) to the DEP assembly behavior of CNTs.

Based on the underlying mechanism of dielectrophoresis which can not readily be revealed experimentally under an optical microscope, theoretical modeling has been employed with several optimizing techniques for DEP assembly of CNTs. Accompanying the theoretical work, detailed experimental investigations have also been performed on all optimized methods. While dielectrophoretic assembly has been intensively investigated through tuning different process parameters, the effort of this thesis contributes to advancing the state-of-the-art DEP in the following three areas:

- By analyzing the relationship between the electrode geometry/configuration and the DEP assembly behavior of CNTs, the shaping electrode technique proposed in this thesis offers a novel strategy for high-precision control over CNT positioning necessary for parallel fabrication of nanoelectronic devices. The proposed scheme is implemented to assemble multiwalled carbon nanotubes (MWNTs) onto electrodes with controllable precision and yield. Two different electrode configurations were suggested for direct assembly of sophisticated nanostructures for practical device applications, where individual MWNTs are anchored across on-chip electrodes or cantilevered electrodes.

- Floating-potential electrodes facilitate DEP assembly by modifying the electric field through selective capacitive coupling. Such an optimizing process is evaluated with respect to its potential to enable bottom-up, low-defect CNT assembly. Consistent $I-V$ characteristics obtained from four-terminal measurements on the assembled devices demonstrate that each nanotube has been addressed individually with solid electrical contact to the electrodes. These results suggest that MWNT-based nano-devices functioning with negligible effects from contact resistance can be manufactured robustly and efficiently.

- This thesis also brings forward a novel method combining dielectrophoresis and thermophoresis which can improve the throughput and precision of DEP assemblies.
assembly. The advantages of thermally enhanced DEP technique point to the relatively high-speed and high-efficiency of DEP deposition of CNTs whose concentration is insufficient for conventional DEP. This optimization scheme has great potential in building research prototypes of “multi-physics” based directed self-assembly methods for developing next-generation NEMS devices, improving possibility of their large-scale manufacturability and commercialization.

1.5 Thesis Organization

Chapter 1 reviews and analyzes the state-of-the-art advancement of DEP assembly methods and put forth the goal of this thesis.

Chapter 2 introduces the concept of dielectrophoretic assembly, where forces generated on polarizable objects in an electric field are induced to position nanoscale objects (e.g. CNTs) with high spatial precision. A theoretical model considering different parameters that influence the dielectrophoresis process is built in order to analyze the deposition mechanism. Simulations of the CNT motion are carried out to describe the effects of process parameters, serving as a basis for different optimization schemes to be implemented experimentally.

Chapter 3 presents a silicon nanomachining-compatible nanofabrication approach for constructing various carbon nanotube nanostructures via DEP assembly. A shaping electrode method is proposed to achieve precise positioning and controlled alignment of nanotubes in the devices. The applicability of this technique to assembling cantilevered CNTs on three dimensional (3D) protruding nanoelectrode pairs is presented.

Chapter 4 presents a floating-electrode DEP (feDEP) technique to further improve the assembly of individual CNTs by precise control over the deposition location. To enable this level of control, the electric field analysis associated with floating electrodes are discussed. Additionally, experimental investigations were carried out to compare the DEP alignment function of such electrodes and that of conventional DEP electrode setup.

In Chapter 5, based on the assembled nano-architecture using feDEP, four terminal measurements have been performed to study the electrical properties
intrinsic to the MWNTs. This method has the advantages of eliminating the interference effects from the probe/sample interface and realizing accurate electrical characterization. Impedance measurement results on the cantilevered MWNTs deposited on 3D protruding nanoelectrode pairs are analyzed.

In Chapter 6, a hybrid DEP assembly method integrating DEP with thermophoresis has been investigated both theoretically and experimentally. This hybrid method combines the localized nature of dielectrophoretic forces with a more global force field induced by thermophoresis. CNT mobility is numerically evaluated based on DEP forces and thermal forces. Experimental results show that the thermally assisted (temperature gradient induced) DEP technique improves the yield of CNT assembly, which indicates a new perspective in the directed self-assembly of micro/nano objects.

Finally, Chapter 7 summarizes the results of different optimizing techniques of DEP assembly and highlights the key research findings in this thesis. An outlook for future research directions is also presented.
To overcome the challenges in placing nanotubes selectively and accurately with micro- or nano-sized precision, many methods have been investigated to provide the optimum path towards creating CNT-based NEMS devices, including robotic manipulation [61], site-selective chemical vapor deposition [62], fluid flow assembly [55] and dielectrophoresis (DEP) [63]. Among these methods, dielectrophoresis, which combines bottom-up and top-down nanomachining unit processes, in particular, provides an efficient and inexpensive tool for parallel fabrication of high quality carbon nanotube based NEMS devices [64].

However, DEP assembly of nanotubes is fundamentally a stochastic process and often provides results with considerable variations, due to a large number of parameters that are difficult to define or control. While the DEP technique has been used successfully and is still under development, the in situ manipulation of CNTs cannot be readily observed during DEP assembly and the mechanisms underlying the DEP process have not yet been fully elucidated because of the complicated nature of the three-dimensional electrohydrodynamic process.

So far, several efforts have been performed to describe the effects of some process parameters on the DEP assembly behavior of CNTs with respects to specific applications. To discover the ideal condition of CNT assembly on the atomic force microscope (AFM) tip, the immersion time, the gap distance between the tip and the electrode plate, the pulling speed, and the shape of the tip have been investigated [65-67]. It is also found that the concentration of the CNT suspension, the magnitude of the applied voltage, and the duration of the electric field, are significant factors to ensure assembly of CNTs across an electrode gap [68].

In this chapter, the general relationship between the CNT deposition behavior and physical parameters such as the nanotube suspensions, non-uniform electric field and electrode configurations have been investigated theoretically. The DEP force and torque components associated with the first order dipole moments of CNTs are derived, neglecting contributions from the higher order moments. The finite element model (FEM) to simulate the translation and the rotation of the individual CNT is
presented. The simulation results can also be used as guidelines for DEP assembly experiments to controllably locate, align and assemble one dimensional micro/nano materials.

2.1 DEP Theory

Dielectrophoretic nanoassembly is an electrokinetic manipulation process where the interactions between a non-uniform electric field and a polarizable particle are utilized to move the particle in space with nanoscale precision. The non-uniform field strength around the polarizable particle exerts a dielectrophoretic force on the dipole induced within the particle, which drives the particle towards the electric field maximum or minimum (positive DEP and negative DEP). In addition, the resulting torque aligns the particle along the direction of the applied electric field. Figure 2.1(a) illustrates two possible directions of motion of a CNT under dielectrophoresis. Positive dielectrophoresis is used to attract the nanotube with a dielectric constant larger than the medium to the electrodes, whereas negative dielectrophoresis occurs when the nanotube moves away from the electrodes because it has a dielectric constant smaller than the medium.

![Figure 2.1](image_url)  
**Figure 2.1** (a) Dielectrophoresis concept. (b) Diagram of the dielectrophoresis system.
2.1.1 DEP FORCE AND TORQUE

Based on Pohl’s theory [69], the dielectrophoretic forces $F_{\text{DEP}}$ and torques $T_{\text{DEP}}$ can be calculated as

$$ F_{\text{DEP}} = (p \cdot \nabla)E $$

$$ T_{\text{DEP}} = p \times E $$

where $E$ is the electric field and $p$ is the induced dipole moment of the particle. The effective dipole moment of a polarized particle can be expressed as [70]

$$ p = v\tilde{\alpha}E $$

where $v$ is the particle volume and $\tilde{\alpha}$ the complex effective polarisability.

Because both DEP forces and torques are dependent on multiple parameters, such as particle and suspending medium properties and the applied electric field, it is impractical to derive the solutions for all cases [71]. To simplify the computation without losing the essential quantitative nature of the DEP process, the CNT is modeled as a prolate ellipsoid with homogeneous dielectric properties, where $l = a_1$ and $r = a_2 = a_3$ ($a_1$, $a_2$ and $a_3$ are radii along three principal axes of the ellipsoid). A dielectrophoresis system is constructed with two rectangular coordinates as shown in Figure 2.1(b): $x$, $y$, $z$ (corresponding to the electrode axes), $l$, $2$, $3$ (corresponding to three axes of the ellipsoid), and the angle between the electric field and the longest axis $l$ is $\theta$.

The effective dipole moment method is used to compute the force and torque exerted on a CNT being subjected to an electric field. The method is valid provided the length of the dipole is smaller than the typical dimension of the non-uniform electric field, an assumption referred to as the dipole approximation. Both the dipole moment and the complex effective polarisability ($\tilde{\alpha} = 3\varepsilon_n \hat{K}_n$) are a function of orientation of the principal axis $n$ of the ellipsoid ($n = l$, $2$, $3$). The complex frequency dependent factor similar to the Clausius-Mossotti factor is $\hat{K}_n$, and the depolarization factor $L_n$ can be calculated by an elliptical integral [72]
where \( \tilde{\epsilon}_p \) and \( \tilde{\epsilon}_m \) are complex dielectric permittivities of the particle and the surrounding medium, respectively, both given by

\[
\tilde{\epsilon} = \epsilon - i \frac{\sigma}{\omega}
\]  

(2.5)

where \( \epsilon \) is the real permittivity, \( \sigma \) the conductivity, and \( \omega \) the angular frequency.

It is straightforward to derive the dielectrophoretic force on a given rod-like CNT [73]

\[
F_{\text{DEP}} = \frac{1}{2} \text{Re}(\tilde{\alpha}) \nabla |E|^2 = \frac{3}{2} \pi r^3 l \epsilon_m \text{Re}(\tilde{K}_v) \nabla |E|^2
\]

(2.6)

where \( r \) and \( l \) are the radius and length of the CNT, respectively.

The frequency of the applied electric field must be sufficiently high to ensure that the CNT responds only to the time-averaged torque [72]. For the convenience of simulation, only the DEP torque about the \( z \) axis perpendicular to the \( x-y \) plane is considered so that the torque exerted on the CNT in an AC electric field may be calculated using \( E_1 = E \cos \theta \) and \( E_2 = E \sin \theta \) which are the electric field components in the \( n \) direction. By substituting the CNT volume and the complex polarisability, the time averaged torque about the \( z \) axis can be obtained:

\[
\langle T_z \rangle = \frac{9}{2} \pi r^2 l \epsilon_m (L_2 - L_4) E_1 E_2 \text{Re}(\tilde{K}_v \cdot \tilde{K}_s)
\]  

(2.7)

The large aspect ratio of CNTs results in a needle-shaped particle with \( l \gg r \), and the depolarization factors can be calculated as \( L_2 = L_4 \approx \frac{1}{2} \) and \( L_6 \approx \frac{a_s}{a_t} \left[ \ln(\frac{2a_t}{a_s}) - 1 \right] << 1 \). In a similar way, values of \( \tilde{K}_v \) are reduced to a simple form, and the governing equations for the dielectrophoresis process are summarized as [74]

\[
\tilde{K}_v = \frac{\tilde{\epsilon}_p - \tilde{\epsilon}_m}{3(L_4(\tilde{\epsilon}_p - \tilde{\epsilon}_m) + \tilde{\epsilon}_m)} = \frac{\tilde{\epsilon}_p - \tilde{\epsilon}_m}{3\tilde{\epsilon}_m}
\]  

(2.8)
2.1.2 Electrohydrodynamics of CNT Assembly

In addition to the DEP force, the fluid surrounding a moving CNT also exerts a force on it. For a prolate ellipsoidal CNT moving under DEP conditions, the viscous drag force, which is proportional to the relative velocity, retards the CNT movement in all directions. The velocity of any particle of mass \( m \) in a fluid environment can be expressed by Newton’s second law [73]

\[
m \frac{dv}{dt} = F_{\text{DEP}} + f(u - v)
\]  

(2.12)

In this simplified equation, we only consider the DEP force and the viscous force, the latter being determined by the relative velocity \( u - v \). The constant \( f \) is the translation friction factor and depends on a range of parameters such as the particle size, shape and the fluid viscosity \( \eta \). Recalling the Perrin friction factors and hydrodynamic approaches further developed by Hardings and Small [75, 76], the translation friction of a prolate ellipsoid particle moving with respect to each axis can be derived. The average friction factor for a randomly moving ellipsoid particle is generalized and used

\[
\langle f \rangle = \frac{3\pi \eta l}{\ln(l/r)}
\]  

(2.13)

Assuming the particle is initially at rest, the solution to this equation is

\[
v = \left( \frac{F_{\text{DEP}}}{f} + u \right) (1 - e^{-t/(mf)})
\]  

(2.14)

The exponential term describes the acceleration of the particle and has a characteristic time constant \( \tau_a = mf \). Considering the CNT in a viscous medium, the
time scale we utilize in both simulations and experiments is greater than the characteristic time constant so that the carbon nanotube will move at its terminal velocity as soon as it is exposed to the electric field. Without fluidic motion \((u = 0)\), the terminal velocity can be derived as

\[
v_T = \frac{F_{\text{dep}}}{f}
\]  

(2.15)

The rotational motion of the CNT can be solved by combining the electrorotational torque induced by the DEP force and the drag torque characterized by the viscous force. Parameters including inertia moment, angular velocity and rotation friction factor need to be taken into account. Similar to the procedure of deriving the translation velocity, the constant angular velocity of a particle in an electric field is proportional to the torque:

\[
w_T = \frac{T_{\text{rot}}}{f_o}
\]  

(2.16)

The rotational friction factor of the CNT rotating about its centre in \(x-y\) plane can also be calculated by hydrodynamic equations [77]

\[
f_o = \frac{2}{3} \pi \eta \frac{(l^2 + 4r^2)l}{2 \ln \left( \frac{l}{r} \right) - 1}
\]  

(2.17)

Furthermore, it is important to note that when a CNT moves under the dielectrophoresis conditions, the effects of gravity, Brownian motion and electro-osmosis are all negligible. The instantaneous translation velocity is proportional to the instantaneous dielectrophoretic force; meanwhile, the rotation velocity is in direct proportion to the time-averaged dielectrophoretic torque.

2.2 DEP Model

A two-dimensional model for the simulation of CNT assembly by dielectrophoresis is presented here. The simulation is based on the effective dipole moment method and considers both the DEP force and viscous drag force from the dielectric medium. The dipole model is proposed to calculate the dielectrophoretic force acting on the CNT in a non-uniform electric field [44]. Note that when the size of the particle is comparable
to the characteristic length of the electric field, the effective dipole moment method is expected to give less accuracy than other hybrid approaches [78, 79]. However, under the DEP conditions used in the current work, it should be sufficient to use the effective dipole moment model because it shows the correct trends in the force variation and provides a good approximation at a fraction of the computational costs of the other methods. The characteristics of the DEP conditions and the physical properties of the CNTs and the dielectric media [43, 80, 81] used in the numerical calculation are summarized in Table 2.1.

The induced charges are assumed to be located along the centerline of the CNT. Based on the induced-charge densities, expressions to calculate the electric fields and electric field gradients are formulated. During simulation, the DEP force and torque are calculated to predict the dynamic motions and trajectories of an individual CNT. Considering a basic electrode pair (the structure of which is shown in Figure 2.2(a)), the spatial distribution of the electric field across the two electrodes is derived by solving Poisson’s equation with classical finite element method (based on a commercial software COMSOL).

The magnitude of the electric field and its gradient are linearly interpolated between adjacent grids, which ensures that the DEP force and torque exerted on a CNT at any given position in the fluid can be deduced (Figure 2.2(b-f)). Taking into account the derived DEP force/torque and the fluid drag force, both translational and rotational motion of the CNT suspended in the fluid dielectrically interacting with the applied electric field can be simulated. The simulation program is updated in a series of time intervals (1 µs), which is much larger than the calculated characteristic constant (1.7×10^{-10} s), to ensure that the CNT moves and rotates all the time with its terminal velocity [66]. Each calculation step of the finite element modeling is shown in Figure 2.2, while Figure 2.3 presents a typical simulation result of the dynamic motions of a CNT.
### Table 2.1 Variables and corresponding values used in simulations

<table>
<thead>
<tr>
<th>Variables</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT length</td>
<td>$l$ 2.5 $\mu$m</td>
</tr>
<tr>
<td>CNT radius</td>
<td>$r$ 10 nm</td>
</tr>
<tr>
<td>Electrical potential</td>
<td>$V_{p-p}$ 2~8 V</td>
</tr>
<tr>
<td>Electric field frequency</td>
<td>$f$ 5 MHz</td>
</tr>
<tr>
<td>Metallic CNT conductivity</td>
<td>$\sigma_{m-CNT}$ $10^8$ S/m</td>
</tr>
<tr>
<td>Semiconducting CNT conductivity</td>
<td>$\sigma_{s-CNT}$ $10^5$ S/m</td>
</tr>
<tr>
<td>Vacuum permittivity</td>
<td>$\epsilon_0$ $8.854 \times 10^{-12}$ F/m</td>
</tr>
<tr>
<td>Metallic CNT permittivity</td>
<td>$\epsilon_{m-CNT}$ $10^4 \epsilon_0$</td>
</tr>
<tr>
<td>Semiconducting CNT permittivity</td>
<td>$\epsilon_{s-CNT}$ 2.5 $\epsilon_0$</td>
</tr>
<tr>
<td>DMF permittivity</td>
<td>$\epsilon_{DMF}$ 38.25 $\epsilon_0$</td>
</tr>
<tr>
<td>IPA permittivity</td>
<td>$\epsilon_{IPA}$ 18.3 $\epsilon_0$</td>
</tr>
<tr>
<td>DI water permittivity</td>
<td>$\epsilon_{DI}$ 80 $\epsilon_0$</td>
</tr>
<tr>
<td>DMF conductivity</td>
<td>$\sigma_{DMF}$ 6 $\mu$S/m</td>
</tr>
<tr>
<td>IPA conductivity</td>
<td>$\sigma_{IPA}$ 6 $\mu$S/m</td>
</tr>
<tr>
<td>DI water conductivity</td>
<td>$\sigma_{DI}$ 5.5 $\mu$S/m</td>
</tr>
<tr>
<td>Dynamic viscosity of DMF</td>
<td>$\eta_{DMF}$ $0.92 \times 10^3$ Pa·s</td>
</tr>
<tr>
<td>Dynamic viscosity of IPA</td>
<td>$\eta_{IPA}$ $1.96 \times 10^3$ Pa·s</td>
</tr>
<tr>
<td>Dynamic viscosity of DI water</td>
<td>$\eta_{DI}$ $0.89 \times 10^3$ Pa·s</td>
</tr>
</tbody>
</table>
Figure 2.2 Various stages of the finite element analysis during DEP modeling. (a) Contour plot of the electrical potential distribution. (b) Vector plot of the electric field. (c) Contour plot of the electric field magnitude. (d) Vector plot of the DEP force. (e) Contour plot of the DEP force magnitude. Letters A and B label the locations of two opposing electrodes.
2.3 PROCESS PARAMETERS FOR DEP ASSEMBLY

Control over the process parameters including the initial conditions of suspensions and the induced electric fields is crucial for successful DEP deposition of individual CNTs on micro/nano electrodes. In this section, the influences of these process parameters are investigated to analyze the assembly behavior of CNTs under the dielectrophoresis.

2.3.1 CNT SUSPENSION

The concentration of CNTs is the most important parameter among the initial conditions of the CNT suspension. It has been demonstrated that the density or the number of CNTs assembled across the electrode gap increases with the increase in the CNT concentration in the fluid [82]. For single nanotube to be deposited across one electrode pair, which is most desirable for practical applications, the CNT concentration has to be controlled within a certain range, beyond which no tube or multiple tubes will be deposited. Before DEP experiments are carried out, it is prerequisite to ultrasonicate the CNT suspension to maintain a homogeneous dispersion. A recent study, which uses conductance measurement to evaluate the electrical characteristics of assembled CNTs, indicates that CNTs tend to form
aggregates or bundles in the non-ultrasonicated suspension [83]. It is therefore, important to disperse the nanotubes as evenly as possible in the suspension.

In addition to the CNT concentration, contaminants (e.g. surfactants) from the suspension can adhere to the wall of CNTs, which hamper the contact between CNTs and electrodes [41, 84]. Therefore, it is important to exclude such interferences in order to achieve reliable electrical characterization/diagnosis of the assembly results.

2.3.2 DIELECTRIC PROPERTIES OF THE SYSTEM

From Equation (2.4), it is important to note that $\hat{k}_r$ represents not only the magnitude but also the direction of the DEP force. Depending on the dielectric properties of the particles and the fluids, and the frequency of the electric field, the force exerted on the particle can be in either the negative or the positive direction of the electric field gradient. Based on this concept, electric field and DEP force distributions for different types of particles are investigated. When a particle having higher dielectric permittivity than the fluid is present, the electric field is deformed near the particle into denser field lines because current can readily flow through the higher conductivity particles (Figure 2.3(a)). On the other hand, when particles of lower dielectric permittivity are present, the distribution of the electric field is perturbed in a way that the field lines are repelled from the particle (Figure 2.3(b)).

![Electric field distributions in a fluid in the presence of particles of different dielectric properties. (a) The particle has a higher dielectric permittivity than the fluid. (b) The particle has a lower dielectric permittivity than the fluid.](image)
2.3.3 Non-uniform Electric Field

There is a threshold value of the electrical potential that is required to ‘catch’ the nanotube from its suspension [82], which accounts for the observable assembly behavior. It has been demonstrated that the yield of individual CNT deposition increases with increasing electric field strength in a certain potential range. Beyond that, the deposition yield decreases because of an increasing probability of attracting large amounts of CNT impurities blocking the gap [85, 86]. Another parametric study showed that large scale deposition of individual MWNTs can be achieved by deliberately mixing an alternating current (AC) field with a direct current (DC) field, suggesting that the AC field serves to selectively attract the nanotubes while the DC field serves to ensure individual deposition [40].

![Logarithmic plot of the dependence of the real part of $\tilde{K}_s$ on the AC frequency for metallic and for semiconducting CNTs. While metallic CNTs experience positive DEP force at all frequencies, semiconducting CNTs experience the negative DEP force at higher frequencies.](image)

**Figure 2.5** The logarithmic plot of the dependence of the real part of $\tilde{K}_s$ on the AC frequency for metallic and for semiconducting CNTs. While metallic CNTs experience positive DEP force at all frequencies, semiconducting CNTs experience the negative DEP force at higher frequencies.

According to Equation (2.4), $\tilde{K}_s$ is directly proportional to the velocity of the nanotube driven by the DEP force. Figure 2.5 presents the plot of the real part of $\tilde{K}_s$ as a function of the AC field frequency for semiconducting and metallic CNTs that are
2.5 μm in length, 20 nm in diameter and suspended in different fluids: N, N-Dimethylformamide (DMF), DI water and isopropanol (IPA). For metallic CNTs, the real part of the \( \tilde{K} \) factor is positive at all frequencies for all fluids. At low frequencies, metallic CNTs have much larger values of the DEP force and velocity. For semiconducting CNT, at frequencies higher than 170 MHz, it experiences a negative DEP force and starts to move in the opposite direction. This frequency is called the “turnover frequency”. The difference in the turnover frequencies between different fluids is determined by the conductivity and permittivity of the nanotube as well as the dielectric properties of the fluids [66]. Note that the magnitude of \( \tilde{K} \) for the semiconducting nanotubes in the negative DEP region is very small, in other words, the negative DEP force is generally weaker for manipulating nanomaterials [81].

### 2.3.4 Electrode Configuration

The effect of electrode configuration is highly relevant to the application of DEP-assembled CNT-based structures. It is demonstrated that perpendicular electrodes have better control over the CNT’s location and direction than parallel electrodes [43]. For the case of CNT-attached probes that are frequently used in AFM because of their sharpness [47, 71], a number of studies have been carried out to reveal the relationship between the curvature of the AFM tip and the yield of single-CNT attachment by DEP [87, 88].

Understanding the dielectrophoretic behavior of CNTs associated with various electrode geometries is essential for realizing the successful assembly of sophisticated nanostructures [89]. This dissertation demonstrates the capacity of the DEP method to precisely assemble and align individual CNTs onto electrodes of a variety of geometries. In Chapter 3, a simple, reproducible and efficient shaping electrode method will be demonstrated for assembling individual CNTs. Strategies for further improvement of CNT alignment are also suggested and analyzed.

### 2.4 Summary

Dielectrophoresis is a powerful tool for the assembly of nano-objects such as CNTs through the dipole-induced translation and rotation of the objects along the electric
field lines. Here, theoretical considerations and a simulation model are presented to
describe electrohydrodynamics of CNTs during the DEP assembly process. Numerical calculations of the DEP force and torque are developed based on the
effective dipole model. By balancing the dielectrophoretic and hydrodynamic
contributions, the simulation results presented here have provided insights into the
mechanism of DEP assembly and have demonstrated the feasibility of using DEP
assembly as a reliable technique for fabrication of CNT-based nanostructures.

Various parameters determining the DEP process have been investigated in detail. The magnitude of the applied voltage regulates the strength, distribution and gradient of the electric field. The permittivity and conductivity of the CNTs and the liquid media, along with the AC frequency, determine the DEP force and torque through the polarization factors. The number of CNTs that can be assembled onto an electrode pair depends on the CNT concentration in the fluid. Though CNTs are used as examples, the modeling method for the DEP assembly presented throughout this chapter is also applicable to other nanomaterials, in particular those of nearly one-dimensional morphology. Fabrication of complex nanosystems by assembly of various materials using this method can therefore be addressed.
3  **SHAPING ELECTRODES FOR CONTROLLED DIELECTROPHORETIC ASSEMBLY**

Many techniques have been explored to address the challenges in developing CNT-based NEMS devices with reliable fabrication in a controlled fashion [55, 62, 90]. A parallel dielectrophoretic assembly approach, using electric fields to manipulate and position CNTs [35, 59, 63], is an important bottom-up technique that paves the way for mass production of sophisticated NEMS devices.

![Figure 3.1 CNT-based mass sensors. (a) On-chip nanotube resonator with an attached mass at the center of nanotube length. (b) Cantilevered nanotube resonator with an attached mass at the tip of nanotube length. (Images adapted from Reference 91)](image)

Recent efforts to use dielectrophoresis (DEP) for CNT assembly have primarily concerned optimizing several parameters in DEP, including AC voltage and frequency, properties of the solution, electrode shape/configuration and spacing size [57, 82]. Of these efforts, modifying electrode configuration is highly effective in that it provides direct control over the electrohydrodynamic behavior of CNTs such as their orienting, moving and depositing. Depending on the selective arrangement of electrodes and their predesigned geometry, a number of assembled nanostructures that
are differentiated in condition (on-chip/cantilever) and function (probing/sensing) can be achieved [71]. Some configurations, representative of the versatility of this unique technique in forming fundamental nanoscale building blocks [91], are illustrated in Figure 3.1.

### 3.1 Local Shape of On-chip Electrode Pair

To achieve high-precision dielectrophoretic assembly of carbon nanotubes for next generation NEMS, a technique of shaping the local geometries of nanoelectrodes is investigated both theoretically and experimentally. Motion trajectories and positions of CNTs assembled on the electrodes are predicted based on calculated DEP forces and torques. Both simulation and experimental results show that the local geometries of two opposing electrodes significantly affect the precision and robustness with which CNTs can be deposited.

We simulate the motion trajectory and the position of CNTs deposited on electrodes based on a variety of electrode geometries. In the simulation, the force and torque components of CNTs are associated with fluid interaction simplified as Stokes drag [72], allowing for determination of the CNT velocity in the fluid. Based on this, CNT motion in suspension can be described and the relationship between the geometry of electrodes and dynamic motions of CNTs can be studied. First, the influence of the local shape of an on-chip electrode pair is investigated, enabling the improvement of the precision and yield of CNT assembly and the ability to define conditions for achieving a desired configuration of CNTs.

#### 3.1.1 Results

The motion of a CNT is mainly determined by the DEP force and torque, which is influenced by the electric field and its gradient. The most direct way to modify the distribution of electric field and gradient is by changing the geometry of electrodes. We conducted simulations for diverse electrode shapes, such as rectangular electrode pairs, round electrode pairs and hybrid (a combination of rectangular and round) electrode pairs.

The modeling procedure is similar to the process outlined in Chapter 2. First, the
magnitude of the electric field and its gradient between two opposing electrodes were simulated [92]. This is followed by taking all the key factors involving the DEP force, the torque and the fluid viscous force into account. At the last step, both translational and rotational motions of the CNTs are simulated. The simulation program is updated with a time interval of 1 µs, with the assumption that the CNT moves and rotates with its terminal velocity at all time intervals [66]. Figures and videos generated during simulations are analyzed in detail.

For all cases, two opposing electrodes are placed in a 4 µm × 4 µm area, in which a CNT (length 2.5 µm, radius 20 nm) moving in DMF is to be assembled. The initial position of the CNT is set as follows: taking the center of the area as the origin, the coordinates of the center of the CNT is (-0.93 µm, -0.1 µm), and it forms an angle of 45° about the x-axis. Physical properties of a metallic CNT and DMF are listed in Table 2.1. Based on the chosen AC frequency, properties of the CNT and the suspending medium, the CNT experiences positive DEP, and, thus moves toward the region of the highest electric field gradient and aligns parallel to the electric field line.

In the case of the round electrode pair (see Figure 3.2I), each electrode has a semi-circular head with a radius of 500 nm and distance between two closest points of 1.6 µm. Figure 3.2I(a) illustrates the motion trajectory of the CNT, while Figure 3.2I(b) presents both the translational and the rotational motion. It appears that the DEP force of the round electrode pair is centralized between the protruding semi-circle heads. The calculated DEP torque and the variation of the CNT acceleration and velocity predict that the CNT moves to and deposits across the protruding semi-circles of the round electrodes, as shown in Figure 3.2I(c).

In the case of the rectangular electrode pair (Figure 3.2II), the two rectangular electrodes (1 µm × 1 µm pads) are 1.6 µm apart. Differing from the case of the round electrode pair, the DEP force increases gradually and reaches a maximum at the electrode corners. The simulated CNT motion trajectories are shown in Figure 3.2II(a-b). The assembled CNT finally bridges the electrode corners, as depicted in Figure 3.2II(c).
The results shown in Figure 3.2 I and II are based on electrode pairs whose geometries have to be perfectly defined during the electrode fabrication process involving E-beam lithography (EBL). However, one problem caused by “proximity effects” is commonly observed in EBL, which leads to geometrical deviation of the fabricated structures from the designed mask. The proximity effects caused by forward and backward scattering of electrons within the EBL resist can occur within a range of a few microns. Therefore, in the third case (Figure 3.2III), an example accounting for the proximity effects in practical operation is presented, in which one electrode is not perfectly semi-circular at the head but instead bears a flat segment due to over-exposure of pixels near the tip. It is evident that one end of the deposited CNT
is not located in the midpoint of the upper electrode but shifts to the edge of the flat segment. These results suggest that the flat segment formed by inaccurate pattern transfer leads to observable field distortion and modifies the assembly behavior.

**Figure 3.3** (a) SEM image of the CNT crossing two protruding points of a pair of round electrodes (Inset: the simulation result as shown in Figure 3.2 I(c)). (b) SEM image of the CNT bridging a protruding point and a corner of the hybrid electrode pair (Inset: the simulation result shown in Figure 3.2 III(c)). (c-d) SEM images of several CNTs depositing on parallel electrode pairs. (e-f) SEM images of a CNT deposited in the vicinity of two sharp corners.

Experimentally, DEP assembly of CNTs using diverse electrode shapes has been performed and examples of reproducible results are presented in a series of SEM images. As shown in Figure 3.3(a), the assembled CNT crosses two midpoints of the round electrode pair, whereas in Figure 3.3(b), the CNT bridges the corner of the flat segment of the right-hand-side electrode and the midpoint of the electrode on the left. This observation is consistent with the simulation results (see insets of Figure 3.3(a-
In addition, for plate-like electrode pair, a CNT experiences equally distributed attractive forces between the gap, directing it to deposit across any two points of the electrodes. In Figure 3.3(c-d), it is evident that several CNTs are assembled onto electrodes in a parallel manner. Experimental examples illustrating the impact of sharp electrode corners are shown in Figure 3.3(e-f). It is found that the CNT inclines to deposit onto sharp corners, which inconsistent with the simulation results (Figure 3.2II(a-c)).

In general, for electrode pairs with sharp regions on the electrodes, e.g. corners of rectangular electrodes and electrode tips, the DEP force is intensified toward these regions, contributing to preferable CNT assembly there. For round electrode pairs which have a smooth profile, the DEP force attracts the CNT to the midpoint of the semi-circle head, and the alignment of CNTs occurs precisely at the central line linking the electrodes.

### 3.2 Local Shape of Protruding Electrode Pair

Among various CNT-based devices, protruding CNT cantilevers have been widely used in NEMS. Over the past 20 years, cantilevered CNTs have mainly been used as a routine imaging tool for atomic force microscopy [93, 94] because of their small diameters, robust mechanical properties and the possibility of chemical and biological functionalization. For example, the CNT probes hold potential for facilitating molecular-scale investigation of biological experiments including the desorption of molecules into a cell’s interior [91, 95].

A variety of sensor applications of cantilevered CNTs have been explored based on different sensing mechanisms. Typical examples are mass [96, 97], strain, pressure and flow [98, 99], force and displacement [100, 101], and chemical gas sensors [102, 103]. In particular, the working principle of CNT-based mass sensors is based on the fact that the resonant frequency of the CNT is sensitive to its mass, the change of which due to the attachment of materials under probing causes a shift of the resonant frequency [56, 104, 105]. Besides, variation of the electrical conductance of CNTs
caused by loading of target species or molecules provides another type of signal for the application of CNT sensors [106].

Recently, it has been demonstrated that cantilevered CNT devices could contribute to achieving CNT-based electromechanical data storage devices [107, 108]. Such memory devices, which have the advantages of high data storage density and low power consumption, employ CNTs as both molecular device elements and molecular wires for the read-write operations.

Conventional methods to integrate individual protruding CNTs into devices with high reproducibility require nontrivial efforts. Several groups have reported that cantilever CNTs can be generated by complicated catalyst patterning and subsequent nanotube growth under chemical vapor deposition (CVD) conditions [93]. Note that using this scheme it is difficult to perform lithography on non-flat surface [109]. Nanomanipulation using single or multiple tool tips provides an alternative towards integrating nanotubes onto microcantilevers and complex three-dimensional structures while maintaining good control over the CNT position [61, 110], dimension and orientation [111]. However, complex multi-probe systems that allow two or more scanning probe tips to be moved independently inside a scanning electron microscope are both expensive and incapable of performing parallel assembly of CNTs.

Practical commercialization of CNT cantilever-based devices is possible only if controllable deposition of CNTs on a large scale (i.e., in a parallel fashion) can be achieved in the manufacturing of the devices. In this section, a novel method of arranging single nanotubes into three-dimensional (3D) protruding nanostructures utilizing shaping electrode technique is presented. An array of L-shaped needle-like electrodes has been used to assemble vertically aligned CNT cantilevers. In this way, all constituent nanotubes can simultaneously be assembled between two electrodes, therefore leading to parallel production without losing precision in CNT positioning. This method can provide a simple, effective and versatile way to fabricate three-dimensional CNT-based cantilever structures [95].

3.2.1 Standard Operating Procedure

The standard operating procedure (SOP) for the assembly of cantilevered CNTs onto protruding nanoelectrodes is presented in this section. The nanofabrication process
integrates “bottom-up” DEP nanoassembly with conventional “top-down” unit processes such as lithography, metal deposition, dry/wet etching and lift-off. The individual steps in this process are shown in Figure 3.4 which provides details of the operating procedures. Note that this method can be generalized for assembly of one-dimensional nano-objects besides the CNTs that are shown in the figure.

**Figure 3.4** Procedures of assembling cantilever CNT structure onto protruding nanoelectrodes. (a) Definition of the nanoelectrode structure by E-beam lithography, metal deposition and lift-off. (b) Open the window by removing SiO$_2$ with RIE. (c) Protruding nanoelectrodes obtained by precise dicing and selective KOH etching. (d) Optical image and SEM image of as-fabricated protruding nanoelectrodes. (e) DEP assembly of CNTs from a suspension. (f) The CNT assembled via DEP.
3.2.1.1 Defining the Protruding Nanoelectrodes

A reproducible method to fabricate ultra-small protruding electrode pairs with attributes of nanometer gaps and widths is proposed and described here in detail. The resulting electrode consists of one metallic bilayer (e.g. 85 nm thick gold/15 nm thick chromium) and one layer of silicon dioxide ($\text{SiO}_2$) underneath. This method has the capability of tuning the mechanical properties of the nanoelectrode pairs by adjusting the etching conditions [112]. With the favorable engineering of the local geometry, precise control over the CNT integration into the protruding electrode pairs can be achieved.

The first step involves photolithography and metal deposition to define the 15 nm thick chromium and 185 nm thick gold contact pads after lift-off. The metallic contact pads are necessary for generating the electric fields for dielectrophoretic assembly. In the second step, E-beam lithography is employed to generate nanoelectrode pairs (150-200 nm in width) with a 200 nm separation. Meanwhile, alignment markers are also placed for chip dicing, allowing the chip to be cut precisely to expose the protruding nanoelectrodes. The last step is to lithographically pattern a soft etch mask of Poly(methyl methacrylate) PMMA to protect the electrodes from reactive ion etching (RIE). Following the RIE removal of the SiO$_2$ layer between the two electrodes, the chip is then placed in a 30% KOH solution kept at 70 $^\circ$C for 10 minutes to etch away the underneath silicon layer. This treatment makes the electrodes extend over the edge of the chip. The fabrication procedure is summarized in Table 3.1.
Table 3.1 Parameters used for defining the protruding nanoelectrodes.

<table>
<thead>
<tr>
<th>Main procedure</th>
<th>Process steps</th>
<th>Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Definition of electric contact pads by UV lithography</td>
<td>Spin coating of photo resist</td>
<td>1.5 µm of AZ 5214E</td>
<td>AZ 5214E is an image reversal photoresist.</td>
</tr>
<tr>
<td></td>
<td>UV lithography exposure</td>
<td></td>
<td>Exposure of the contact pads pattern</td>
</tr>
<tr>
<td></td>
<td>Resist development</td>
<td>AZ 726 for one minute 20°C</td>
<td>Formation of the contact pads pattern</td>
</tr>
<tr>
<td></td>
<td>Metal deposition</td>
<td>15 nm Cr and 185 nm Au</td>
<td>E-beam evaporation of metals</td>
</tr>
<tr>
<td></td>
<td>Lift off</td>
<td>40 mins NMP 50°C</td>
<td></td>
</tr>
<tr>
<td>Definition of nanoelectrode pairs by E-beam lithography</td>
<td>Spin coating of EBL resist</td>
<td>220 nm of PMMA layer</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Raith 150 EBL exposure</td>
<td>Aperture:10um Votage:30kv 300mJ/cm²</td>
<td>Exposure of the nanoelectrode pairs pattern</td>
</tr>
<tr>
<td></td>
<td>Resist development</td>
<td>MIBK : IPA (1: 3) for 58 seconds</td>
<td>Formation of the nanoelectrode pairs pattern</td>
</tr>
<tr>
<td></td>
<td>Metal deposition</td>
<td>15 nm Cr and 85 nm Au</td>
<td>E-beam evaporation of metals</td>
</tr>
<tr>
<td></td>
<td>Lift off</td>
<td>40 mins NMP 50°C</td>
<td></td>
</tr>
</tbody>
</table>
**Definition of etching gaps by E-beam lithography and Reactive ion etching**

| Spin coating of EBL resist | 180nm of PMMA layer | The PMMA layer acts as the soft etching mask to protect the electrodes from the following reactive ion etching.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Raith 150 EBL exposure</td>
<td>Aperture:10µm Voltage:30kv 200mJ/cm²</td>
<td></td>
</tr>
<tr>
<td>Resist development</td>
<td>MIBK : IPA (1: 3) for 58 seconds</td>
<td></td>
</tr>
</tbody>
</table>
| Reactive ion etching with RIE80 | CHF3/O2 with flow rates of 30 cm³/min and 20 cm³/min | Removal of the SiO₂ layer between electrodes
| Dicing chips with the wafer dicing saw Disco DAD 321 | Precisely cutting the chips along the predefined markers | Nanoelectrodes are 3-5 µm away from the edge of chips.
| UV Ozone | 10 minutes | Removal of the residual mask
| KOH etching | 30% KOH at 70°C for 10 minutes | Removal of the silicon under the electrodes from the side of the chip

**Formation of the protruding nanoelectrode pairs**

| Reactive ion etching with RIE80 | CHF3/O2 with flow rates of 30 cm³/min and 20 cm³/min | Removal of the SiO₂ layer between electrodes
| Dicing chips with the wafer dicing saw Disco DAD 321 | Precisely cutting the chips along the predefined markers | Nanoelectrodes are 3-5 µm away from the edge of chips.
| UV Ozone | 10 minutes | Removal of the residual mask
| KOH etching | 30% KOH at 70°C for 10 minutes | Removal of the silicon under the electrodes from the side of the chip
3.2.1.2 Nano-object Assembly onto Protruding Nanoelectrodes

Nano-objects are deposited onto the protruding nanoelectrodes by dielectrophoretic assembly. As an example, multiwalled carbon nanotubes (MWNTs) are suspended in N,N-dimethylformamide (DMF) which is subjected to ultrasonication for 6 hours to ensure homogeneous dispersion. The CNT concentration in the suspension is maintained at 1 µg/ml, meaning that on average only one tube at a time has a probability of being close to the protruding nanoelectrodes for assembly. The tubes are deposited by applying an AC peak-to-peak voltage of 5.5 V between the opposing electrodes. A 5 MHz frequency is found to be optimal for the alignment of MWNTs [40]. In a typical DEP experiment, a 10 µl drop of the CNT/DMF suspension is placed to immerse the whole chip, on which the DEP conditions are applied for 100 s, followed by washing with DMF and drying with N\textsubscript{2}. The assembly parameters related to the target nano-object and the nanoelectrode structure are discussed in the next section based on both theoretical modeling and experimental results.

3.2.2 Results

Numerical simulations of the electric field-induced assembly of CNTs have been carried out using a finite element method. The modeling results provide the fundamental framework for a comprehensive understanding of the deposition mechanism, which is critical to the improvement of the assembly precision. Details of the simulation methods can be found in Chapter 2.

It has been shown previously in this chapter that the electrode design has a direct impact on the positioning accuracy that can be achieved in DEP assembly. Figure 3.5(a-b) presents the simulation results of the electric field contours for the protruding nanoelectrodes with different geometric features, e.g. L-shaped and parallel electrode configurations. In the case of parallel electrodes (Figure 3.5(a)), the electric field maxima occur at the protruding tips of both electrodes while the electric field distribution is quite uniform between the electrode fingers. The electrokinetic behaviors of the CNTs are simulated by implementing the finite element model into Matlab programs. The preferred assembly region predicted by the simulation, as shown in Figure 3.5(c), strongly resembles the electric field distribution contour.

For the L-shaped electrode configuration, the location of the field maxima is
confined to the gap between the two electrode tips, as highlighted in Figure 3.5(b). Figure 3.5(d) shows the simulated dielectrophoretic force field and motions of the CNT. Under this configuration, the direction of CNT motion is identical to that of the DEP force, causing the CNT to align at the electrode tips with one end free-standing.

**Figure 3.5** (a) Contour plot of the magnitude of the electric field vector for parallel electrode configuration. (b) Contour plot of the magnitude of the electric field vector for L-shaped configuration. (c) Moving trajectories of a CNT for parallel electrodes. (d) Moving trajectories of a CNT for L-shaped electrodes. (e) A CNT assembled onto parallel electrodes. (f) A CNT deposited onto the electrodes with L-shaped configuration. Red arrows indicate the direction of the electric field; green dots cover the region where the magnitude of the DEP force is above the threshold value for assembly; blue dots cover the region where the DEP force is greater than 5 times the threshold force.
It is important to note that the dielectrophoretic velocity taken (or force experienced) by small objects cannot be measured easily. Brownian motion can dominate particle dynamics for small (e.g. sub-micron) particles. Based on a probabilistic method of calculating force, an expression is derived that can be used to estimate the force required to produce observable movement of a sub-micron particle against random Brownian motion [73].

In the absence of any deterministic force, the CNT undergoes only Brownian motion. After a time $\delta t$, the position of the particle is represented by a normal distribution with standard deviation $\sigma$. There is a 99.7% probability that the CNT will be found within $3\sigma$. When it is subjected to the DEP force, as discussed, the CNT moves at a steady-state velocity given by $v = \frac{F_{\text{DEP}}}{f}$. Over the time interval $\delta t$, the CNT displacement is $\delta x = v \cdot \delta t$. According to the statistics and probability theory, an observable deterministic threshold force can be defined as the DEP force producing the displacement of $3\sigma$ after the time interval $\delta t$,

$$|F_{\text{thr}}| = 3 \frac{f \sigma}{\delta t}$$

(3.1)

Substituting the value of $\sigma$ in this equation, $|F_{\text{thr}}| = \sqrt{18kTf}$, where $k$ is Boltzmann’s constant.

Through the above equation and employing all values, the observable deterministic force for the given CNT is computed as $10^{-10}$ N, which is the threshold DEP force necessary to produce an observable movement of the CNT in the preserved Brownian motion. This threshold DEP force defines the statistical tendency of the CNT deposition and provides insights into the electrohydrodynamics aiding in the design of experiments. In Figure 3.5(c-d), the DEP force magnitudes ($F_{\text{DEP}}$) are marked by green and blue dots (green dots: $5 \times 10^{-10}$ N $> F_{\text{DEP}} > 10^{-10}$ N, blue dots: $F_{\text{DEP}} > 5 \times 10^{-10}$ N), of which the green dots mark the region where $F_{\text{DEP}}$ can overcome Brownian motion and produce deterministic movement of the CNTs.

Figure 3.5(e-f) show SEM images of the MWNTs assembled onto the protruding electrodes with the same configuration as modeled in panels ‘c’ and ‘d’. It is evident that the alignment of MWNTs occurs precisely in the fashion predicted by numerical simulations. More importantly, the implementation of the shaping electrode method to
diverse electrode configurations enables a considerable degree of control over the assembly behavior of CNTs, making possible the large-scale manufacturing of complex hierarchical CNT-based nanostructures. While the MWNT deposition is expected to occur in the region where the DEP force is beyond the threshold value (as illustrated by the blue and green dots in Figure 3.5(c-d)), supplementary SEM images of nanotubes contacting two biasing electrodes are shown in Figure 3.6. Thus, these results demonstrate that modifying the electrode shape/configuration can precisely control the region in which CNT assembly occurs, leading to significant improvement in the efficiency and accuracy of CNT deposition.

3.2.2.1 Electrical Measurement

Cantilevered MWNT devices have been fabricated based on the configuration demonstrated in Figure 3.4, from which an individual CNT is positioned on top of two protruding electrodes that directly serve as the biasing and measuring terminals. Figure 3.6(c) shows the two-point resistance of one MWNT example. Five sets of data are selected from 10 successive measurements with the microprobes placed on the contact pads and a recording time interval of 10 s. Electrical measurements of these fabricated nanostructures not only allow us to study their electrical transport properties but also help to identify the role of contact resistance in the performance of CNT-based NEMS devices, which will be elucidated in the following section. From the IV characteristics of the assembled cantilever MWNTs, it is evident that the resistance of the MWNT is in the range of 90-100 KΩ. The values measured here are comparable to the data of the CNT devices fabricated by other assembly methods such as CVD growth of nanotubes. Therefore, the results in the present study further supports the effectiveness of the shaping electrode DEP method for the site-selective positioning of individual nanotubes between two electrical contacts.
Figure 3.6 (a-b) SEM images of CNTs assembled onto protruding nanoelectrodes with L-shaped configuration. (c) Electrical measurement results of the assembled CNT/electrode structure presented in (b).

3.2.3 DISCUSSION

The measured resistance comes mainly from the MWNT/Au contact interfaces and the MWNT itself. The calibration measurements also indicate that the resistance between testing microprobes and Au electrodes is in a range of several ohms. The influence of this resistance on the measured nanotube resistance, therefore, is negligible. Joule heating with power ($P = I^2R = V^2/R$) occurs at the interface region between the nanotube and electrode surface while electrical carriers pass through the nanotube channel. For instance, when a 1 µA electric current $I$ is applied, the power $P$
applied onto the interface will range from 0.01 to 100 µW corresponding to a contact resistance of $10^4$–$10^8$ Ω. This power is high enough to anneal the nanoscale interface region, and even to burn out nanotubes.

It is important to note that in the electrical measurement, the 10 s measuring time interval indicates a long biasing time of current flowing along the MWNT. One interesting observation showed that an assembled MWNT has been welded to one of the electrodes after seven measuring cycles, as supported by the SEM image of a welded MWNT shown in Figure 3.7(b). One possible reason could be that the high contact resistance causes local Joule heating and the metal grain boundaries to reflow at the MWNT-electrode interface, resulting in an increased contact area and a reduced resistance. A direct consequence is that the van der Waals interaction between the MWNT and the electrode is significantly enhanced, causing the nanotube to remain welded to the gold pad even after the bias is removed.

This effect of local Joule heating to reduce the contact resistance at the CNT/metal interface has been previously reported [113, 114]. The $I$–$V$ characteristics and the electrical resistance of the MWNT before and after the local annealing are shown in Figure 3.7(a) and Figure 3.7(c), respectively. It is evident that there is a step-like decrease in the resistance (measured to occur at cycle 7) accompanied by an ohmic-type behavior beyond this event, which can be explained by the reduced contact resistance resulting from Joule heating at the CNT/Au contacts. As a result, the resistance of the whole structure decreased by 12–17% from the original resistance.
Figure 3.7 (a) $I-V$ curves before and after Joule heating. Seven cycles of electric current flowing through the device induces local annealing at the CNT/metal interface. (b) A CNT welded onto the metal electrode after accumulatively long biasing time. The high power dissipation at the CNT/electrode contact causes the metal to reflow and extend the interface area. (c) The resistance curve of the device exhibits a step-like decrease during Joule heating.

3.2.4 Failure Mode Analysis

Common failure modes in this assembly scheme includes the absence of CNTs, presence of graphitic carbon impurities impairing the device performance, presence of redundant tubes (Figure 3.8(a)) and CNTs that come into poor contact with the electrode (Figure 3.8(b-c)). It has been reported that using the similar CNT suspensions for DEP assembly, the fill-factor (defined as the percentage of electrode pairs on which CNTs are deposited) is in the range of 60–70%, while 40% represents the assembly of individual CNTs in perfect contact to the metal electrodes [63].
Figure 3.8 Device failure modes. (a) Multiple CNTs assembled on the same protruding electrode pairs. (b-c) Nanotubes with improper contacts. Instead of bridging the metal electrodes from above, the CNTs lie underneath the electrodes. (d) Misalignment of a CNT at the undesirable region resulting in assembly failure.

In addition, another failure mode associated with these devices pertains to the complete misalignment of MWNTs as shown in Figure 3.8(d). Instead of a cantilever configuration, the nanotube deposited on two metal contacts situates nearly perpendicular to the protruding electrode because of the intricate initial condition in the MWNT suspensions and the intrinsic low accuracy of conventional DEP assembly method. The complete misalignment of nanotubes is an important failure mode that reduces the yield of nanotube assembly suitable for device applications.

3.3 SUMMARY

In this chapter, the mechanisms of dielectrophoretic manipulation of CNTs onto different electrode-pair configurations have been investigated both theoretically and experimentally. Simulation results of the electric fields, DEP forces and torques and the dynamic motions of individual CNTs have been analyzed and compared with experimental results. It is found that CNT deposition is significantly affected by the
electrode geometry and configuration, which determine the area of the maximum electric field gradient. The shaping electrode DEP method has been proposed for improved positioning and alignment of CNTs during assembly by pre-designing the shape of electrode pairs and the spacing between neighboring electrodes. The methodology presented here is completely general and is expected to be applicable to the assembly and characterization of other one-dimensional nano-objects, contributing to manufacturing of next generation NEMS devices.

The validity of the shaping electrode DEP method has been demonstrated by the fabrication of cantilevered CNT devices containing protruding nanoelectrodes. The experimental results of the CNT assembly behavior are in excellent consistence with the modeling results. Importantly, these results seem to satisfy the requirements for large-scale manufacturing of the nanotube-based cantilever devices. Taking advantage of the high-precision positioning of the CNTs, the as-assembled CNT/electrode nanostructures can find applications in ultra-sensitive measuring, molecule/cell manipulation and memory devices with fast response and low power consumption. While the major interest here is manipulating CNTs via dielectrophoresis, it is likely that the fundamental findings presented here can be transferred to DEP assembly of non-carbon based nanowires, nanorods or nanobelts.
4 FLOATING-ELECTRODE DIELECTROPHORETIC ASSEMBLY OF MWNTS ONTO PROTRUDING NANOELECTRODES

A new floating-electrode dielectrophoresis (feDEP) approach for optimizing the assembly of individual carbon nanotubes is presented in this chapter. Precise control over the deposit location is achieved by using nanoelectrodes held with electrical floating potential. Together with the investigation of electrode geometry effects demonstrated in Chapter 3, the feDEP approach provides a comprehensive capability for realizing sophisticated electrode architectures expected to enable the manufacturability and commercialization of next generation NEMS.

Floating electrode DEP method can be used to realize both on-chip and cantilevered CNT devices depending on the nanoelectrode configuration. Further processing by controlled shell removal at different segments along the length of an on-chip MWNT structure created NEMS devices based on inter-shell displacement mechanisms, such as bearings, switches and sensors [35, 63, 115]. Apart from numerous applications as stated in Chapter 3, another possible research area of cantilever nanostructures relate to investigate the electromechanical properties of assembled MWNTs. It has been demonstrated that the inner shells have significant contributions to multi-shell electrical conduction, so the electron transport in the MWNT is sensitive to telescoping shell movement [116, 117]. Therefore, appropriately constructed nanostructures, by using a combination of DEP assembly and telescoping, can help to understand the electromechanical coupling between individual shells within a MWNT [112]. The significance of these architectures is further enhanced by the ability to reduce contact resistance with four-point measurement, which is also important for the use of MWNTs for electrical interconnect and nanoelectronic applications.
4.1 Concept and Theory

Many proposed nanoelectromechanical systems (NEMS) require precise positioning of individual carbon nanotubes. However, direct manipulation of single CNTs using scanning electron microscope (SEM) or transmission electron microscope (TEM) feedback is a complex, time-consuming and low-yield process [118]. For batch fabrication of CNT-based devices, dielectrophoresis is more preferable. However, undesirable configurations of the assembled CNTs often form because the effective DEP forces are limited to the region near electrodes. For example, cantilevered contacts were found on the electrode corner because of unevenly distributed DEP forces. Considerable efforts have been made to optimize the DEP assembly approach. Several groups have demonstrated that floating-electrode dielectrophoresis (feDEP) can result in electric field and DEP force distributions that differ from conventional DEP, thus creating new possibilities for accumulating or isolating nanoobjects [119-122]. Inspired by these previous efforts, a hybrid approach combining the floating-electrode DEP mechanism with shaping electrode theory is proposed to offer a new perspective in improving the precision and maneuverability of CNT assembly [71, 122].

Floating-electrode dielectrophoresis differs from conventional DEP assembly of nano-objects in that it uses conductive but electrically floating elements to affect the imposed electric field. This technique is schematically illustrated in Figure 4.1(a). When the passive elements are placed between two biasing electrodes, they undergo polarization induced by the electric field, and the actual potential at each floating electrode is dependent on the applied voltage.

In the case of feDEP assembly, capacitive coupling is the main mechanism to exert electric potential across the floating electrodes. It usually occurs at high frequency when the impedance between active electrodes and floating electrodes is significantly reduced, allowing for biasing distinct electrodes without inter-electrode bonding wires [119]. The floating electrodes are assumed to be ideally polarizable, i.e., the free charge flow from the electrodes to the fluid is neglected. Chemical reactions at the electrode surface can be an important consideration in the determination of the electrode polarization. However, spectroscopy measurements of
the impedance between active and floating electrodes [123-125] show that impedance decreases as frequency grows, because the Helmholtz double layer at the metal-liquid interface vanishes. Therefore, polarizable floating electrodes is a reasonable simplification, and potential values vary linearly between two active electrodes [126-128]. For example, due to the symmetry of the structure shown in Figure 4.1(b), floating electrode B is expected to be at a potential that is one third of the applied external voltage.

Based on the electrical potential values of every electrode, finite-element models (FEM) developed using batch programs in COMSOL are used to compute the electric field distribution for two different electrode configurations. Figure 4.1(b) shows electric field vectors represented by red arrows and the magnitude of the electric field represented by a contour plot. Note that the regions appearing in red represent the location of field maxima in the plots. In the presence of electrically floating electrodes, the orientation and strength of imposed electric fields are modified, and the electric field strength gradients are increased, allowing for a dramatic extension of the range in which the nanoobjects experience an observably deterministic DEP force.

Figure 4.1 (a) Layout of the multi-electrode system employing active and floating electrodes. (b) Plot of electric field between activated electrodes A and D without floating electrodes. (c) Plot of electric field between activated electrodes A and D with floating electrodes B and C. Arrows indicate the electric field direction.
4.2 Floating-electrode DEP approach

In the floating-electrode DEP regime, all electrodes impact the electric field. Precisely defined alignment of CNTs has been observed in the assembly, and the proposed feDEP scheme has been validated theoretically. The activation scheme requires that only two electrodes are active, the others being electrically floating. DEP experiments have been carried out on multiple electrodes, among which two electrodes are activated by 5 MHz, 7.5 V_p-p sinusoidal signals. MWNTs (20-50 nm diameter, 1-5 µm length, arc-produced from MER Corp.) and N, N-dimethylformamide (DMF) are used to prepare the MWNT suspension. Meanwhile, finite element analysis (FEA) has been performed to derive the electric field strength and gradient in the presence of floating electrodes. MATLAB is used to simulate the DEP force distribution and CNT motion. Adopting similar code as presented in Chapter 2, a MWNT was modeled as a prolate ellipsoid. Dielectric constants and conductivities of a metallic CNT and DMF suspension were selected from Table 2.1. The applied voltage and frequency are consistent with experimental parameters. Due to their capacitive coupling to the active electrodes, floating electrodes are modeled as equipotential conductors undergoing polarization in the external field.

Figure 4.2(a) shows the electric fields and DEP force distribution generated by two parallel active electrodes (conventional DEP), where the highest field strength and the largest DEP forces appear at the edges of the active electrodes (see inset). When the CNT experiences positive DEP force, it moves toward the region with the largest electric field gradient and aligns parallel to the field direction. For the given initial position, the assembled CNT finally contacts only one electrode. Consistent with modeling results, DEP experiments revealed the deposition of cantilevered CNTs onto the corner of one electrode (Figure 4.2(c)).

According to the theory of floating-electrode DEP, introducing conducting and electrically floating objects can change the electric field orientation and strength. Moreover, floating electrodes smooth the local DEP force distribution so that abrupt changes in forces are suppressed, thus reducing the possibility of cantilevered CNTs during DEP processes [129]. In Figure 4.2(b), another electrode serves as a floating electrode between two parallel electrodes, which affects the electric field and DEP
force fields in the multi-electrode system. The DEP forces have peak values at the edges of both the activated and the floating electrode (see inset), making the CNT prone to bridge the three electrodes. Similar results have also been observed experimentally. As shown in Figure 4.2(d), the CNT crosses three parallel electrodes that are perpendicular to the CNT orientation.

![Simulation and experimental results showing (a, c) a CNT in cantilevered contact with one electrode and (b, d) a CNT bridging three electrodes with the central one held at a floating potential. Insets: DEP force distributions on the electrode edges.](image)

**Figure 4.2** Simulation and experimental results showing (a, c) a CNT in cantilevered contact with one electrode and (b, d) a CNT bridging three electrodes with the central one held at a floating potential. Insets: DEP force distributions on the electrode edges.

Although the CNT assembly results in the presented experiments (Figure 4.2(c, d)) might be interpreted as arbitrary cases, a simply modified electrode configuration, consisting of two long active electrodes and one short floating electrode, offers additional proof of the efficacy of the feDEP approach. In Figure 4.3(a, b), it is evident that two distinct assembly behaviors occur at the regions with and without the floating electrode. Multiple cantilevered CNTs are deposited on two outer electrodes, while an individual CNT bridges three electrodes with the middle electrode maintained at a floating potential. In Figure 4.3(c, d), other configurations employing the floating-electrode DEP scheme include four- and five-electrode architectures, both of which exhibit a single CNT perfectly bridging all nanoelectrodes.
Figure 4.3 (a, b) Distinct assembly behaviors are observed by varying the floating electrode length. (c) CNT assembly with two floating electrodes. (d) CNT assembly with three floating electrodes (Image (d) courtesy of Arunkumar Subramanian).

It is important to note that a multi-electrode system containing passive electrodes extends the range of effective DEP forces beyond the proximity of two active electrodes without increasing the gap and the electric field. This compensation technique improves process metrics such as yield and precision by decreasing the possibility of misaligned or improperly contacted MWNTs on multiple electrodes. The feDEP technique thus enables the creation of complex electrode architectures and can be an important tool for batch-fabrication of nanosystems.

4.3 DEVICE STRUCTURE AND FABRICATION PROCEDURE

In addition to improving the alignment of nanotubes on multiple electrodes, the multi-electrode system can be used for controlled the positioning of individual CNTs in a defined region, associating the floating-electrode DEP method with the shaping-electrode technique [35]. The major portion of the tube has contacts with four nanoelectrodes, while the remaining is fully suspended in air. The contacts serve as ‘DEP contacts’ to generate electric/force fields during CNT assembly and can be
subsequently used to perform four-terminal electrical measurements (referred to Chapter 5). Moreover, electromechanical characterization and investigations of useful features of the NEMS devices can be achieved by integrating these devices into electrical circuits and electron microscopes (SEM or TEM) [130]. Such devices have the potential for use in industrial applications such as mass, force and resonant-pressure sensors [8, 131, 132]. They can also serve as the tools for fabricating basic components for assembly of future nanorobots.

The device fabrication procedure is similar to the process outlined in Chapter 3 and is highlighted in Figure 4.4. The hybrid nanofabrication paradigm includes a bottom-up DEP assembly step and conventional top-down processes such as lithography, metal deposition, lift-off and etching. First, four separated metallic electrodes (85 nm thick Au/15 nm thick Cr) are defined using E-beam lithography. This is followed by reactive ion etching (RIE) to remove the SiO$_2$ layer in the vicinity of nanoelectrodes (Figure 4.4(b)). The chip is then precisely cut along predefined markers and placed in 30% KOH solution for 10 minutes to remove the Si substrate, so that the etching starts from the edge of the chip, as shown in Figure 4.4(c). As-fabricated protruding nanoelectrodes are generally 200 nm wide and are separated by 200 nm gaps, which consist of a parallel part and an L-shaped part. The L-shaped four-finger electrode design optimizes the dielectrophoretic assembly of nanomaterials attributed to the shaping electrode approach and feDEP technique (Figure 4.4(d)). Moreover, the protruding nature of the nanoelectrodes facilitates the investigation and characterization of the electrical as well as mechanical properties of the assembled materials. Optical and SEM images of fabricated protruding nanoelectrodes with different tip shapes are shown in Figure 4.4(e-f).
**Figure 4.4** Protruding nanoelectrode fabrication procedures. (a) Definition of nanoelectrodes by E-beam lithography, metal deposition and lift-off. (b) Nanoscale window created by EBL and RIE. (c) Protruding nanoelectrodes obtained by precise dicing and selective KOH etching. (d) Nanomaterial (a MWNT here) assembled by floating-electrode DEP. (e, f) Optical and SEM images of protruding nanoelectrodes with diverse design of tips.
4.4 RESULTS

4.4.1 FEM MODELING

In this section, the feDEP approach has been implemented onto four spatially separate nanoelectrodes to achieve direct assembly of MWNTs (see Figure 4.5). Both the local nanoelectrode shape and the feDEP activation scheme influence the CNT positioning precision. The electrode configuration consists of a parallel region and an L-shaped region (Figure 4.5(f)). Due to this configuration, activating any two electrodes at a time induces independent electric field distributions at the parallel part and the L-shaped part, which gives rise to distinct patterns of CNT deposition.

First, numerical modeling developed using COMSOL and MATLAB are used to explain the nanoassembly results from different activation schemes. It is shown that the L-shaped region of four-finger nanoelectrodes is better suited for assembling cantilevered CNTs as compared to parallel configurations. and the configuration has potential for assembling nanoelectromechanical systems such as scanning probes [94], nanomanipulation tools [95] and sensors [99, 133] with atomic-to-nano scale resolution, because of the unique protruding configuration and remarkable physical properties of the assembled CNTs. However, the positioning accuracy also depends further on initial conditions of MWNTs, as well as the deviation of the fabricated nanostructures from designs during fabrication (e.g. E-beam lithography process and aggressive wet-etching).

The simulation results from the five activation schemes are shown in Figure 4.5, where the electric field vectors are expressed as red arrows, and the DEP force magnitude ($F_{\text{dep}}$) is marked by green and blue dots (green: $5 \times 10^{-10}$ N > $F_{\text{dep}}$ > $10^{-10}$ N; blue: $F_{\text{dep}}$ > $5 \times 10^{-10}$ N). The potential deposition regions are highlighted in grey. The threshold DEP force is calculated to be $10^{-10}$ N based on Equation (3.1) [73]. Beyond the threshold value, the deterministic DEP force produces an observable movement of the CNT in the suspension.
Figure 4.5 Simulation results of five activation schemes of floating-electrode DEP performed on a four-finger electrode structure with L-shaped tips. (a) Electrodes I and II are activated. (b) Electrodes I and III are activated. (c) Electrodes I and IV are activated. (d) Electrodes II and III are activated. (e) Electrodes III and IV are activated. (f) Typical nanoelectrode tip design consisting of L-shaped and parallel regions. From (a) to (e), red arrows indicate the direction of the electric field, green dots represent the DEP force whose magnitude is above the threshold DEP force and blue dots represent the DEP force greater than five times of the threshold force.

In Figure 4.5(a), electrodes I and II are activated while electrodes III and IV remain floating. In the parallel region, the deterministic DEP forces occur on the edges of electrodes I and II, while in the L-shaped region they exist at corners of the top three tips. However, the direction of the electric field in L-shaped region is opposite. Since DEP torques are responsible for the CNT rotation and alignment along the electric field, conflicting rotational motion occurs within that area. This activation scheme is, thus, excluded because of the unstable CNT movement caused by the opposite electric field direction at the L-shaped part. This tendency is further
accentuated in Figure 4.5(e), which exhibits another example of activating two adjacent electrodes.

Different from the previous activation scheme, electrodes I and III are activated in Figure 4.5(b) to extend the deterministic DEP force region to the gaps between electrodes I and IV and electrodes II and III in the L-shaped region. Moreover, the electric field directions are identical for both regions. Under this condition, the assembly of a MWNT can be controlled to occur predominantly on four electrodes in the L-shaped region, which highlights the suitability of this activation scheme for assembling MWNT structures with free-standing ends.

Figure 4.5 (c) illustrates another activation scheme for the electrodes I and IV. DEP forces are centralized between the upper two tips in the L-shaped region, but the electric fields are in an opposite direction. Nevertheless, observable deterministic DEP forces with sub-maximal intensity (green dots) are evenly distributed in the parallel region, and the electric fields are in the same direction. Besides the DEP force as the main factor to influence CNT motion, the DEP torque determines the orientation of the CNTs during the hydrodynamic process, which gradually rotates CNTs following the electric field orientation. Under this activation scheme, the assembly of CNTs is more likely in the parallel region, which is undesirable for NEMS devices requiring MWNTS with free-standing ends.

The last case of activating two neighboring electrodes II and III is useless for the assembly of MWNTs via the feDEP technique, as shown in Figure 4.5(d). In either the L-shaped or the parallel region, the distribution of observable DEP force fails to cover four electrodes. Moreover, the electric field is extensively non-uniform. As a result, the CNT experiences vacillating attraction and undergoes poor alignment in the proximity of protruding nanoelectrodes, leading to few opportunities for assembly.

4.4.2 Floating electrode DEP assembly results

Using the floating-electrode DEP technique, two among five activation schemes contribute to nanostructures consists of a MWNT bridging four nanoelectrodes while remaining fully suspended and flat in the gaps between them. Schematics of four-anchored nanostructures and the corresponding experimental results are shown in Figure 4.6.
Figure 4.6 Experimental results of floating-electrode DEP assembly. (a) Schematic illustration of the CNT assembled on the parallel region of the nanoelectrodes. (b) SEM images of the MWNT bridging four parallel fingers suggesting the potential of this technique for batch fabricating devices engineered by piecewise shell etching. (c) Schematic illustration of the CNT assembled on the L-shaped tips of the nanoelectrodes. (d) SEM images of the MWNT deposited at the L-shaped region. Insets (1) and (2) show high magnification images taken with a stage tilt for observing the encircled contact interfaces, complementary to the top-view.

By applying an AC electric field to the outer electrodes I and IV and keeping the two inner electrodes electrically floating (referred to Figure 4.5(c)), one can assemble a single MWNT bridging four fingers electrodes at the parallel region (Figure 4.6(a)). An SEM image of the assembled structure is shown in Figure 4.6(b), illustrating a nanotube in contact with both biasing electrodes I and IV and floating electrodes II and III. The metal pads located at different segments of the CNT have versatile functions such as electrical contacts, mechanical anchors or heat sinks for piecewise shell etching by joule heating. It has been demonstrated that this structure has a number of potential applications. Using piecewise shell-engineering, ultra-low power electromechanical switches can be realized by electrostatically controlling the movement of the CNT cores and, thereby, modulating the inter-segment conductivity.
The configurational stability and frequency spectrum of these constructs have been reported in a previous study [134].

Another architecture, a representative example of which is shown in Figure 4.6(c, d), is comprised of a CNT contacting four fingers in the L-shaped region. Figure 4.6(c) schematically illustrates one device realized in the manner of biasing electrodes I and III (referred to Figure 4.5(b)). It is evident that the nanotube deposits at the L-shaped region and attaches to four metallic contacts, as shown in Figure 4.6(d). One important aspect that requires careful observation is the contact condition between the CNT and nanoelectrodes from SEM images showing the top-view of nanostructures, as illustrated in the encircled areas of Figure 4.6(d). The small contact areas between the nanotube and the L-shaped tips and the graphitic defect attaching to the nanotube outer-shell interfere electron scattering during SEM imaging, result in difficulties in determining detachment or contact within the limits. From the high magnification images shown in the insets of Figure 4.6(d), the existence of contacts are confirmed with a stage tilt of 15 degrees under SEM. Moreover, this was confirmed by I-V electrical measurements. It is obvious that the apparent noncontact is an imaging artifact and does not impede successful device operation.

Recently, similar architectures for four-point measurements of MWNTs have been developed by standard microfabrication methods [135], however, their electrodes cannot fulfill characterization of MWNTs shorter than four microns. Our fabricated cantilever device is promising in investigating the electromechanical properties of sub-micron objects. Also, since four-point measurement eliminates the influence of the electrical contact resistance at the metal-semiconductor interface [136], this nanostructure realizes precise electrical measurement regardless of the contacting area and contact type in various possible NEMS devices.
4.4.3 Failure modes analysis

Figure 4.7 Device failure modes. (a) Misaligned CNT due to inaccurate DEP assembly. (b) A CNT attached to the backside of the protruding nanoelectrodes. (c) A CNT with insufficient length to cross all four electrodes. (d) A CNT not contacting the top metal layer of electrodes. (e) A CNT with one end touching the SiO$_2$. (f) A CNT with a structural imperfection (kink).

Apart from the favorable architectures that are suited for diverse applications in MWNT-based NEMS devices, undesirable nanostructures can result from nanofabrication and DEP assembly due to imperfections such as structural kinks, imperfect tubes and misalignment. Devices representative of different failure modes are shown in Figure 4.7: (1) misalignment of CNT due to the DEP inaccuracy (Figure
4.7(a)), (2) CNT assembled on the backside of the nanoelectrodes because of their typical protruding configuration (Figure 4.7(b)), (3) imperfect tube with a short length bridging only two of four electrodes (Figure 4.7(c)), (4) CNT attached to the sidewalls of the nanoelectrodes due to DEP inaccuracy (Figure 4.7(d)), (5) CNT with one end contacting the SiO$_2$ residue because of misalignment of the soft mask during RIE, (6) CNT with a kink that is partly thinned. Although process control capabilities (including the shaping electrode method and the floating DEP technique) demonstrated within this effort represent the current state-of-the-art, further advances are needed, both to prevent these failure modes and to improve the yield and precision of DEP assembly.

4.5 **SUMMARY**

The effects of floating potential electrodes on dielectrophoretic assembly of CNTs have been investigated. Both theoretical modeling and experiment results indicate that floating electrodes extend the DEP force field for improving the alignment of CNT in a defined space. A multi-electrode system has been proposed in conjunction with a sophisticated shape design, allowing for the tunable deposition of CNTs in either vertical or horizontal directions. The floating-electrode DEP strategy expands the geometric limit of conventional dielectrophoresis and paves the way for optimizing DEP assembly of CNT-based NEMS device.
5  **Electrical Characterization of MWNTs Using Four-Terminal Measurement**

Carbon nanotubes (CNTs) have attracted much interest since their discovery in 1991, particularly because they could, as promising building blocks, lead to advances in miniaturization of microelectronic devices [137-139]. The utilization of CNT-based devices in practical applications remains challenging, partially because of complex characterizing procedures of each device. The interactions that occur at interfaces between non-carbon materials and CNTs represents a substantial issue of characterizing nanodevices and has been studied theoretically and experimentally [140-142].

Previously, electrical characterization of CNTs was often performed using nanorobotic probes [143-146], which requires manually pushing the probe to the CNT with undetermined forces. Moreover, it can only provide two electrical contacts to one nanotube, which makes it almost impossible to separate the effects of the contact at the probe/nanotube interface from the electrical properties of the NTs. To study the electrical properties intrinsic to the CNT [136, 147], a four-point probe technique is desired to eliminate the effects of the probe/sample contact and to enable accurate electrical characterization of NTs.

The conventional four-point probe method is designed to perform high resolution sheet resistance measurements by approaching and contacting the probes to a sample surface e.g. a Germanium sheet [147]. Recently, the four-point probe method has proven effective for measuring materials with curved shapes, such as semiconducting/metallic nanowires [148, 149] and multi-walled carbon nanotubes [150, 151]. For this purpose, multiple-probe instruments have been widely employed for four-terminal measurements [152]. Dohn [153] used movable microcantilevers that served as contacting electrodes, whereas Ebbesen [150] and Schoenenberger [154] formed metal electrodes on top of CNTs by focused-ion beam and evaporation, respectively. Some reported novel multi-probe instruments composed of four parallel insulating cantilevers were fabricated by conventional silicon processing technique.
ELECTRICAL CHARACTERIZATION OF MWNTS

[155-157].

In this chapter, we demonstrate that the four-finger protruding nanoelectrodes introduced previously can offer fast, reliable and nondestructive electrical characterization of CNTs. Individual CNTs contacting four probes were investigated in detail by measuring voltage as a function of the fixed current, with two of the contacts acting as current source and two others measuring the potential difference [148, 154].

5.1 NANOSTRUCTURE FOR FOUR-TERMINAL MEASUREMENT

To date, nanorobotic manipulation offers controlled positioning and precise integration of CNTs into NEMS with a short turn-around time and micro-to-nanometer resolution. This approach requires pretreatment of CNTs and other processes (e.g. manually pick-and-place [135, 150, 154], functionalization [158, 159] and post-fabrication of top layer contacts on NTs [153, 160]) that hinder the mass production of CNT-based devices.

One typical example of mounting MWNTs onto protruding nanoelectrodes via nanorobotic probes is shown in Figure 5.1. Four-finger nanoelectrodes serve as four terminals in the electrical measurements allowing for studying the intrinsic properties of carbon nanotubes and other nanoscale one-dimensional structures. It is evident that the nanotube was bent when it made contact to the electrodes as shown in Figure 5.1(b).

Figure 5.1 SEM images showing typical nanorobotic manipulations. (a) Probes pick up a single nanotube and approach the protruding nanoelectrodes. (b) The nanotube was deformed from its original shape. (Images courtesy of Kaiyu Shou)
To avoid damage or deformation of NTs by nanomanipulation tools and to achieve solid mechanical and electrical contact, both of which affect the electrical properties of carbon nanotubes [150], it is convenient to directly assemble NTs onto the protruding nanoelectrode structures by dielectrophoresis [86]. Using floating-electrode dielectrophoresis [40, 86] described in Chapter 4, NTs can be successfully assembled on the as-fabricated protruding nanoelectrodes with high-precision alignment and reasonable reproducibility [161]. Therefore, four-point probe measurements can be used on the assembled nanostructure for accurate characterization of the electrical properties intrinsic to the nanotube.

### 5.2 Contact Resistance

A primary challenge for commercializing CNT-based devices, with attributes of small size, fast response and low power dissipation, is the high electrical resistance of metal/CNT contacts. At present, the contact resistance between the CNT and the metal electrode varies widely among reported experimental results, which may reflect a combination of inherent contact resistance and external interference such as that introduced by contamination [142, 162].

The electronic properties of contacts are mainly dependent on the contacting area because weak van der Waals bonding gives anomalously small matrix elements for electrons crossing between the metal and nanotube. Surface wetting of different metals affects the nature of contact interface [163]. A large contact resistance has been measured in particular when the nanotube was simply lying on a metal contact without any soldering [154]. Therefore, it is intuitively clear that a large contact area leads to a better electrical coupling.

It has been demonstrated that the absence of Fermi-level states extending through both the metal and nanotube accounts for the generally high contact resistance [162]. Other factors influencing contact resistance include the physical properties of the nanotubes such as their diameter and chirality [139, 140] or structural defects[164].
5.3 **CONCEPT OF FOUR-TERMINAL MEASUREMENT**

In order to compare two-point and four-point electrical measurements, the following equation can be used to express the total resistance across a single nanotube for conventional two-point measurement:

\[
R_{2\text{-point}} = 2R_c + R_{NT}
\]  

(5.1)

\[
R_{NT} = \frac{\rho l}{A}
\]  

(5.2)

where \(R_c\), \(\rho\), \(l\) and \(A\) represent the average contact resistance at the biasing electrode, nanotube resistivity, length, and cross-sectional area, respectively.

Figure 5.2(a) shows the principle of electrical four-point probe measurements. Four individual probes contact the device under measurement in a co-linear arrangement. The two outermost probes S1 and S2 serve as current sources, resulting in a current \(I_s\) flowing through the sample. The inner terminals, P1 and P2, are used to measure the potential drop between two points on the sample in a current-less fashion [148]. Thus the four-probe resistance is \(R = V / I_s\).

![a](image1.png) ![b](image2.png)

**Figure 5.2** (a) Schematic diagram of a four-probe measurement on a sample. Terminals S1 and S2 source a current, and the potential difference is measured across P1 and P2. (b) Schematic diagram of a four-terminal measurement performed on the as-fabricated protruding nanoelectrodes. In this way effects of the nanotube/metal interface are eliminated.

A schematic diagram of the four-point probe method is shown in Figure 5.2(b), illustrating four nanoelectrodes in contact with a single nanotube. The resistance of
the sample can be measured without contact interference via the four protruding electrode terminals, regardless of whether the contact type is ohmic or Schottky.

5.4 RESULTS

The electrical properties of multiwalled carbon nanotubes are investigated on four protruding nanoelectrodes as presented in Chapter 4. The electrodes are 100 nm thick, 200 nm wide and 2 µm long. The electrode pads were biased specifically for the purpose of DEP deposition of individual MWCNTs. Based on the floating-electrode DEP method, an individual MWNT could be assembled to directly attach to electrodes at desired positions. MWNNTs and DMF were used to make the MWNT suspension of concentration 1 µg/ml. A more detailed description of the suspension preparation is provided in Chapter 2. A droplet of CNT suspension was placed on the chip, to which an alternating electric field (7.5 V_p-p, 5 MHz) was applied.

After precisely assembling MWNTs in the L-shaped region of the nanoelectrodes, the two- or four-terminal resistances at specific positions along the nanotubes are measured with a DC probe station (Karl Suss PM8) which provides DC measurements and records the I-V curves. Via the four needles from the probe station, an electric current from 0 µA to 1 µA is driven through the two outmost electrode terminals while the voltage drop at the two inner pair is measured.

The SEM image of the assembled nanostructure is shown in Figure 5.3(a), where the four electrode fingers play the same roles as current source (S1, S2) and measuring terminals (P1, P2) as suggested in Figure 5.2(a). Typical I-V plots are shown in the six results selected at the same intervals from twenty consecutive measuring cycles for an individual MWNT-based device. Figure 5.3(b) exhibits a linear, ohmic behavior indicating the nanotube is in good physical contact with the electrodes. The measured resistance spectrum lies in the 135-145 kΩ range. It is also evident in the SEM image that the electrode spacing between the inner measuring pairs is 200 nm. The nanotube cross-sectional area A can be calculated by $\frac{\pi(d_o^2 - d_i^2)}{4}$, the outer and inner diameters ($d_o$ and $d_i$) are observed to be 10 nm and 4 nm, respectively. The average value of the corresponding nanotube resistivity can be calculated as 46.2 µΩ•m. These values of MWNT resistivity lie within the range reported in the literature [153, 165].
The robustness of the four-point probe method was investigated by repeating independent measurements on one MWNT-based device. For each measurement, four needles of the probe station were lifted until no current passed through the MWNT and no bias voltage was observed. They were brought into new contact with the metal pads. Figure 5.3(c) shows the resulting $I-V$ curves of five successive tests chosen from ten independent measurements. The measurement results show no apparent variance for different contact positions and point to an average resistance between $136 \, \text{k}\Omega$ to $142 \, \text{k}\Omega$.

![Figure 5.3](image)

**Figure 5.3** (a) SEM image showing four-terminal measurements on the fabricated nanoelectrodes. (b) $I-V$ characteristics of six measurements selected from twenty consecutive cycles with the probe remaining in contact between measurements. (c) $I-V$ curves recorded during cycles three through seven among ten successive measurements where the probe was lifted between adjacent tests. (d) Five out of ten two-terminal measurements on the same nanostructure with two inner electrodes as both current source and voltage loading points.

Next, two-point measurement results were compared on the same device with the 4-point probe method (Figure 5.3(d)). The electrical resistance and resistivity of the nanotube is obtained by measuring its $I-V$ behavior across the two inner electrode contacts. The average resistance ranged from $209 \, \text{k}\Omega$ to $214 \, \text{k}\Omega$ indicating a resistivity
of 69.2 $\mu\Omega\cdot m$. By merging all the data in Figure 5.4, it is clear that the two-point measurement resistance is generally 60 k$\Omega$ higher than either consecutive or independent 4-terminal measurement results, implying that the contact resistance is in the range of 60 k$\Omega$.

![Figure 5.4](image)

**Figure 5.4** Average resistances obtained on the same nanostructure. Blue: ten successive four-terminal measurements. Green: ten independent four-terminal measurements. Red: ten successive two-terminal measurements.

5.5 **Discussion & Analysis**

The experimental resistivity of MWNTs obtained here is in agreement with results reported previously [153, 165]. However, it was reported that the resistivity can be easily decreased by one or two orders of magnitude [166, 167], which indicates that significant changes in electrical measurements may be caused by undetermined material quality and interlayer separation.

The resistivity of MWNTs is expected to vary in that the intrinsic resistance of CNTs is determined by the diameter, chirality, defect and curvature of the CNTs. In addition, the helicity and number of individual shells also influence the electronic wave packet propagation in disorder-free systems [116]. Different from samples deliberately selected by nanorobotic manipulation under SEM or TEM, CNTs
assembled by DEP often start with variant initial conditions, leading to the deviation of their resistivity from some published results. The remains of catalytic particles in the CNT shells and different structural defects could also influence the measured resistivity [168].

Another reason for the slightly large resistivity of the MWNTs could be that their outmost shell is semiconducting. In fact, an idealized MWNT free of defects can have only one outermost shell in intimate contact with electrodes, and different shells within a single MWNT should randomly alternate between metallic and semiconducting characters. According to [166], the semiconducting outermost shell can be completely depleted of charge carriers and become insulating at positive bias, thus the measured non-zero conductance is purely due to contributions from inner shells, which are weakly coupled through diffusive regime and quantum interference [169]. Since the current flows mainly along individual shells that are well insulated from each other in spite of the narrow shell separation, the contribution of inner shells to the entire conductance behavior is directly connected to inter-shell interactions. The intershell conductivity is found to be consistent with tunneling through orbitals of nearby shells and exhibits considerable temperature dependence [117, 169].

5.6 Summary

A new method has been presented for manufacturing four-point contact, suspended MWNT-based devices using floating dielectrophoresis. This strategy offers an alternative route to realize the assembly of nanostructures on a large scale and provides the possibility for characterizing assembled MWNTs without damage or deformation. The contact-resistance-free electrical measurements of carbon nanotubes indicate the necessity of using the four protruding electrode configuration. Given suitable optimization of the system architecture, the described method should have promising perspectives for mass production of CNT-based NEMS devices and their non-destructive, reliable electrical characterization.
Similar to other “phoretic” transport processes, such as electrophoresis, dielectrophoresis and optophoresis [170], thermophoresis refers to the drift of particles or molecules along temperature gradients. Manufacturing processes based on thermophoresis assume that localized liquid temperature gradients can be established and controlled in a flexible manner [171, 172]. Recent insights stemming from experimental and theoretical investigations have contributed to deeper understanding of the physical mechanisms of thermophoresis, which creates a new way of driving nanoparticles [173]. Fifty years ago, thermal gradients were first applied for particle sedimentation and collection. When a constant temperature difference was applied across the channel, dispersed particles had the tendency to accumulate on the cold side due to thermophoresis. This phenomenon is important for the aerosol technology [174] for collecting and removing particles from laminar gas streams in sampling and cleaning devices [175]. Apart from the aerosol field, the same mechanism can be utilized in various applications, such as, thermal field-flow fractionation [176], DNA extension/accumulation [177-179], and deposition of single-walled carbon nanotubes [180].

Although thermophoresis is often considered as a subtle interfacial effect, it has attracted extensive interest for manipulating particles in fluid [181]. A temperature difference may be introduced by Joule heating induced on metal electrodes [182], local laser heating [183, 184] and infrared absorption [180, 185]. Nevertheless, the optical related techniques pose strict requirements on illumination intensity and wavelength, which prohibits the use of, for example, low-cost laser diodes. Joule heating can be readily implemented on-chip, either by designing the fluid channel for heating and cooling fluids, or by inserting heaters which can increase the liquid temperature of a bulk volume or in a local region.

In this chapter, by incorporating an electrical heating device in the solution, a hybrid DEP assembly method has been realized by integrating thermophoresis. This
technique enables long-distance migration of particles in response to a temperature difference, beyond near-field DEP manipulation. This strategy provides substantial control over the precision and yield of the CNT assembly by properly adjusting the temperature gradient.

6.1 CONCEPT

Thermophoresis is a non-equilibrium cross-flow effect between mass and heat transport, similar to thermal diffusion (the Soret effect) in simple fluid mixtures [186]. It is based on the motion of particles responding to thermal forces arising from a temperature gradient in a gas/fluid media. It was originally explained by the kinetic theory of gases. The higher energy molecules in the hot regions of the medium bombard the particles with greater momenta than molecules coming from the cold regions, thus resulting in the migration of the particles in the direction of decreasing temperature. Thermophoresis also affects particles suspended in a liquid in which a temperature gradient is present. In addition to Brownian motion, a steady drift velocity caused by thermophoresis causes the particles to move from the hot to the cold region. This is similar to applying an external force field to the suspension, such as gravity.

In a discussion of thermophoresis, different regimes have been characterized by the Knudsen number \( (l/a) \), where \( l \) is molecular mean free path of the surrounding medium and \( a \) is the radius of the suspended particle taken as spherical.

In the free molecule regime characterized by a value of \( (l/a) >> 1 \), the particle is so small or the molecular mean free path so large that the particle experiences virtually no influence by the molecular velocities of the surrounding medium. In this case, the thermophoretic force on the particle can be calculated by adding all the impulses transferred to it by the colliding molecules from the surroundings [187].

In the regime characterized by a small Knudsen number \( (l/a) << 1 \), where the particle is large compared with the mean free path, the fluid flow may be described by a continuum model. The thermophoretic force arises from the thermal slip induced by the tangential temperature gradient at the particle-fluid interface. Applying the thermal slip boundary conditions to the Navier-Stokes equation, and taking account of
the frictional slip and temperature jump, Brock has develop the thermophoretic
velocity and force for spherical particles [188]. For dense gases or liquids the concept
of a mean free path is not relevant and it is more appropriate to consider the mean
spacing between atoms or molecules instead [189]. The mean spacing between the
liquid molecules is around an angstrom[190]. Because the carbon nanotubes have
considerably larger dimensions (µm) than the mean spacing of liquid molecules in
suspension, the small Knudsen number regime can be adopted in the hybrid assembly
system for combing thermophoresis and dielectrophoresis.

However, there should be significant discrepancy between the thermophoresis of
spherical particles and that of CNTs. In general, the thermophoretic properties of non-
spherical particles are anisotropic, and the thermophoretic velocity is no longer
collinear with the temperature gradient. Here, the carbon nanotube is to be considered
as prolate spheroid, and the analytical analysis of the thermophoretic motion of the
CNT is presented in the next section.

6.2 THERMOPHORESIS OF CARBON NANOTUBE

In the ‘large particle’ regime (small Knudsen number), Brock has extended the theory
to the solution with additional temperature jump and frictional slip based on Epstein’s
equation [172] of a suspended aerosol sphere with thermal slip [188]. The following
expression was obtained for the thermophoretic force for a sphere-like particle [191],
which is valid for most applications in the field of particle technology.

$$
F_{th} = -9\pi \frac{\eta^2}{\rho T_0} a \left( \frac{1}{1+3c_m \frac{l}{a}} \right) \left( \frac{k_f + c_m \frac{l}{a}}{1+2 \frac{k_f}{k_s} + 2c_m \frac{l}{a}} \right) \nabla T_{\infty} \tag{6.1}
$$

Here, the dimensionless coefficients $C_t$ and $C_m$ account for the temperature jump
and frictional slip at the particle surface, respectively; $a$, the radius of particle; $T$, the
absolute temperature; $\rho$, the mass density; $l$, the mean free path of the fluid; $k_f$, the
thermal conductivity of the fluid; $k_s$, the thermal conductivity of particle; $\eta$ the
viscosity of the fluid; $\nabla T_{\infty}$ the temperature gradient.
Although it is common to estimate the thermophoretic behavior of the non-spherical particles using an ‘equivalent sphere’, the calculation of the equivalent sphere does not take into account the orientation of the particles. In our case, the CNTs are approximated as prolate spheroids immersed in a liquid with arbitrary temperature gradient. The contribution from thermal slip dominates over frictional slip and temperature jump, so the thin layer of fluid at the particle surface moves toward the high temperature side caused by the tangential temperature gradient, allowing for CNT movement in the opposite direction.

The continuum fluid motions related with thermal conduction can be solved by the Navier-Stokes equation in the presence of a temperature gradient and in the absence of external forces. Considering the boundary conditions of thermal slip velocity at the particle/fluid interface, a detailed derivation of the values of the thermophoretic velocities $U$ can be found in [192, 193], in which

$$ U = -\mathbf{m} \nabla T $$

(6.2)

The thermophoretic velocity is a vector composed of longitudinal components and transverse components $U = U_l e_l + U_t e_t$, and $\mathbf{m}$ is the thermophoretic mobility.

Here, $e_l$ and $e_t$ are the unit vectors in the longitudinal and transverse directions with respect to the particles’ axis of revolution; $U_l$ and $U_t$ are longitudinal and transversal components of thermophoretic velocity.

In the following analysis, thermal slip boundary conditions, correct for the physical system, have been applied and approximate expressions for the velocity and temperature equation have been obtained. At low Reynolds number and low Peclet number, the thermophoretic force can be taken as the viscous force, which is derived by integrating the normal component of the pressure tensor over the surface of the particle.

$$ F_{th} = 6\pi\eta(RU_l e_l + RU_t e_t) $$

(6.3)

The definition of thermophoretic mobility is $m_l = U_l/E_l$ and $m_t = U_t/E_t$, where $E_l$ and $E_t$ are longitudinal and transverse components of instantaneous temperature gradient $\nabla T$. 
Analytical formula for the radii of the equivalent sphere ($R_l$ and $R_t$), are given by Brenner and Jennings [194, 195].

\[
R_l = \frac{8a\delta}{3} \left[ \frac{(2-\delta^2)}{\delta^2(1/\delta^2 - 1)^{3/2}} \ln \left( \frac{1+(1-\delta^2)^{1/2}}{1-(1-\delta^2)^{1/2}} \right) - \frac{2\delta}{(1-\delta^2)} \right]^{-1}
\]

\[
R_t = \frac{8a\delta}{3} \left[ \frac{\delta}{(1-\delta^2)} + \frac{(2-3\delta^2)}{\delta^2(1/\delta^2 - 1)^{1/2}} \ln \left( \frac{1+(1-\delta^2)^{1/2}}{\delta} \right) \right]^{-1}
\]

Here prolate spheroids are considered, each with major axis (or half length) $a$ and equal minor axis $b$ with $\delta = a/b \geq 1$. Because the thermophoretic mobilities are functions of thermal conductivities and particle shape, it is possible to simplify the derivation by considering some special cases [192]. Herein, the carbon nanotube can be treated as the limiting case of a needle-like structure of length $2a$ and diameter $2b$. When $a/b \to \infty$ equations for $m_l$ and $m_t$ can be reduced to

\[
m_l = (1 + k^*/2) m_s
\]

\[
m_t = (1 + k^*/2) / (1 + k^*) m_s
\]

The magnitudes of these motilities are normalized by the corresponding thermophoretic mobility $m_s$ of a spherical particle.

\[
m_s = \frac{C_s}{\rho T_0} \left( 1 + \frac{1}{2} k^* \right)^{-1}
\]

where $C_s$ is the thermal slip coefficient and $k^* = k_s/k_f$.

Governing equations for the thermophoretic force on spheroid particles experiencing either longitudinal or transverse temperature gradient can be obtained by Equation (6.4). A number of experimental and theoretical works have provided thermal slip coefficients for various fluid-solid systems [196].
It is of particular interest to calculate the average velocity and force of a group of nanotubes in which particles are suspended with random orientation in the fluid. To apply thermophoresis to the DEP assembly of CNTs, the average results can provide more practical guidance for experimental investigations. For an ensemble of identical, non-interacting spheroids with random orientation-distribution, the average particle force can be evaluated from the longitudinal and transverse motilities [194].

\[ F_{an} = -2\pi \eta (R_mC_m + 2R_mC_T) \nabla T \]  

(6.10)

To investigate the feasibility of thermophoretic manipulation of the carbon nanotubes, a prolate spheroid model has been adopted in the continuum fluid regime subject to the thermal slip boundary conditions. Solving the hydrodynamics and thermophoresis equations in the CNT suspension leads to reliable evaluation of the thermophoretic motions of an independent CNT in response to a temperature gradient. Moreover, to provide valuable experimental guidance, average results of the velocities and forces for a group of non-interacting nanotubes have been attained using longitudinal and transverse mobilities.

### 6.3 Thermophoresis Enhanced Dielectrophoresis of CNTs

With the knowledge that heat in the suspension can increase Brownian motion in the neighboring region, and the imbalanced Brownian motion will transport micro/nano particles to the cooler region, temperature gradients give rise to the large-scale thermophoretic drift of particles. This phenomenon is a potential candidate for manipulating CNTs, and for compensating for important deficiencies in conventional DEP.

Assuming a carbon nanotube initially at rest, the structure instantaneously attains its terminal velocity because the timescale used in simulations and experiments is greater than the characteristic time constant \( \tau_\alpha = \frac{m}{f} \), where \( m \) is the mass of the CNT and \( f \) is the translation friction factor that is a function of a range of parameters including size and shape and fluid viscosity \( \eta \).
According to Newton’s second law, a nanotube of mass \( m \) will move under the influence of the dielectrophoretic force \( F_{\text{DEP}} \), thermal force \( F_{\text{thermal}} \), and the total velocity of the nanotube can be expressed by the following equation

\[
v_{\text{total}} = F_{\text{DEP}} + F_{\text{thermal}}
\]  

(6.11)

Using the thermophoretic force developed for a prolate spheroid particle with arbitrary orientation in fluids (Equation (6.10)) [192], and the well-established equations of the DEP force for needle-like particles (Equation (2.10)) [72, 73], an analytic analysis has been done to compare CNT migration behavior for pure DEP and thermally enhanced DEP.

Figure 6.1 shows the analytical results of the total velocity over the pure DEP velocity \( v_{\text{total}} / v_{\text{DEP}} \) as a function of the normalized initial position \( x/l \) for different values of the temperature gradient. The ratio \( v_{\text{total}} / v_{\text{DEP}} \) represents the relation between nanotube velocities with and without thermal enhancement. For a given temperature gradient, the ratio of the velocities is an increasing function of initial position because \( F_{\text{DEP}} \) vanishes rapidly with growing \( x/l \), while \( F_{\text{thermal}} \) remains constant. For a given initial position the total velocity versus the pure DEP velocity increases with \( \nabla T \), because the thermal force is proportional to the temperature gradient in accordance with Equation (6.11). Modeling results show that an increase of the temperature gradient significantly enhances nanotube mobility.
6.4 APPLICATION & DISCUSSION

6.4.1 TEMPERATURE FIELD

The external resistive heater causes local heating resulting in temperature gradients in the CNT suspension, which in turn generates a body force on the nanotube. The thermophoretic force, written in terms of the temperature gradient, acts in the same direction along the temperature field. To explain the thermophoretic effects on the hydrodynamic behavior of a single nanotube, the Navier-Stokes equation in the heat transfer module with COMSOL software was used. In the model, a gold resistive heater is applied with a DC supply and placed inside a 3 mm hemisphere droplet. The temperature field, temperature gradient, and particle motions were investigated by changing the heat source value. This model permits the superimposition of the dielectrophoretic force, thermophoretic force and corresponding fluid drag force on the mass-less rod-shaped particle.

Three heat transfer regimes are considered in this model. The heat generated in the droplet is transported to the surroundings through radiation, convection, and conduction. Convective heat transfer is enabled inside the droplet. At the droplet’s
THERMOPHORESIS ENHANCED DEP ASSEMBLY

Under these assumptions, a finite element model with the presence of a gold resistive heater has been developed and is shown schematically in Figure 6.2(a). Figure 6.2(b-c) shows the distribution of temperature and temperature gradient of nine equidistance points with the distance to the heat source from 500 µm to 1.5 mm. As seen in Figure 6.2(b), the resulting temperature differences are not large on an absolute scale. Due to the small system dimension, however, the temperature gradients are significant. It is evident that the temperature increases with time before the heat balance is achieved at 90 s, suggesting the droplet maintains a relatively constant temperature gradient. Based on the same DC setting for the resistive heater in real experiments, an infrared thermometer was used to measure the increasing

Table 6.1 Parameters of temperature field modeling

<table>
<thead>
<tr>
<th>Variables</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (DMF)</td>
<td>$\rho_{\text{DMF}}$ 0.944x10³ kg/m³</td>
</tr>
<tr>
<td>Thermal conductivity (DMF)</td>
<td>$k_{\text{DMF}}$ 0.1663 W/(m·K)</td>
</tr>
<tr>
<td>Heat capacity (DMF)</td>
<td>$C_{\text{DMF}}$ 2030 J/Kg·K</td>
</tr>
<tr>
<td>Droplet volume</td>
<td>$v$ 10⁻⁸ m³</td>
</tr>
<tr>
<td>DC supply for heat source</td>
<td>$V_{\text{DC}}$ 1~10 V</td>
</tr>
<tr>
<td>Initial pressure</td>
<td>$p_0$ 10⁵ Pa</td>
</tr>
<tr>
<td>Initial temperature</td>
<td>$T_0$ 300 K</td>
</tr>
<tr>
<td>Thermal conductivity (gold)</td>
<td>$k_{\text{Gold}}$ 318 W/(m·K)</td>
</tr>
<tr>
<td>Molar mass (DMF)</td>
<td>$M_{\text{DMF}}$ 73.9 kg/mol</td>
</tr>
</tbody>
</table>
temperature of a 15 µl droplet. It was found that the increase of the droplet temperature after 100 s is 5 K, which is in agreement with the simulated temperature increase ranging from 1 K to 9 K.

By determining the temperature distribution in the system, the temperature gradient can be determined accordingly. In Figure 6.2(c), the temperature gradients of nine equidistant points increase with time, but they exhibit different slopes for reaching the equilibrium state. Because the temperature gradient distribution is location dependent, the position nearest to the heat source undergoes a constant temperature gradient after 30 s, but the farthest point does not reach the equilibrium state until 90 s.

In contrast to the static thermophoresis with a constant temperature gradient over a channel [188], our system presents a dynamic thermophoresis with a non-uniform temperature gradient along the transverse direction in the droplet. According to Chapter 3, when the nanotube is subjected to an external force greater than $10^{-10}$ N, it has the capability to overcome Brownian motion and begin migration towards the desired electrodes. Based on Equation (6.10), thermophoretic force with regards to the temperature gradient ($10^4$ K/m) in the farthest position is derived as $10^{-9}$ N, which is comparable to the threshold value of observable DEP force. Therefore, thermophoresis can be used to move CNTs in fluid, which extends the limited attraction range of DEP force over a much large area [197]. It is evident that long-range carbon nanotube transport due to thermophoresis, with the assistance of local trapping by dielectrophoresis, can improve CNT assembly efficiency at electrodes.

The particle moving trajectory can be simulated in the model with the knowledge of temperature fields and temperature gradients. Time varying temperature gradients at different initial points lead to distinct velocity fields and motion behavior of CNTs. Figure 6.2(a) shows the trajectories of four NTs residing at equidistant points in the line with $x$ coordinates ($-5\times10^{-4}$ m $~5\times10^{-4}$ m) and $y$ coordinate ($2\times10^{-4}$ m). Although the temperature gradient distribution is not uniform and the thermal force varies during continuous modeling time, the trajectory of the CNTs could be predicted. An interesting observation is that four CNTs all move in the opposite direction of the thermal gradient and arrive at the droplet boundary, indicating a total displacement of 0.5 mm$\sim$1 mm. Therefore, the CNT assembly is facilitated by applying an external
heater if the thermophoretic force is comparable to the DEP force, which offers a new perspective to realize controllable assembly of CNTs over a large area.

![Figure 6.2](image)

**Figure 6.2** (a) Finite element model. Arrow: temperature gradient. Contour: temperature distribution. Moving trajectories of 4 mass-less CNTs under thermophoresis are presented. (b) Temperature distributions of nine equidistant points. (c) Temperature gradient distributions of nine equidistant points. Despite small temperature variations on an absolute scale, large gradients are observed due to the small system dimensions.

### 6.4.2 Thermophoretic Effects

The finite element analysis of the temperature field in the CNT suspension provides a comprehensive understanding of the phenomenon and suggests potential manipulation of CNTs by means of local heating. As we discussed in the previous section, the CNT will move in the direction opposite to the thermal gradient, i.e. from the hot region to the cold region, allowing for migration over a longer distance. A hybrid approach that combines thermophoresis and conventional dielectrophoresis has been investigated both theoretically and experimentally. It shows direct evidence that the thermal force expedites the migration, and, meanwhile, enables the large distance transportation of
CNTs. This method affects the dynamic motion of nanotubes and alters assembly patterns by modulating temperature distributions through controllable resistive heaters on-chip.

Hydrodynamic simulation of the CNTs in the suspension has been performed with an imposed temperature field and electric field. The integration of thermophoretic modeling to the dielectrophoretic modeling adopts the same finite element model, which represents the CNT as a prolate ellipsoid. The fluid flow induced by the density and pressure changes during the heating of the liquid is neglected. The temperature distribution in the suspension is defined by the DC voltage applied to the heater. For instance, with a 4V DC supply, a heater with 20 Ω resistance can generate 1 J of heat. Assuming the heat is diffusive in the suspension, the temperature field and the thermal force at any point can be simulated accordingly.

In an effort to describe the impact of thermophoresis on dielectrophoretic deposition of CNTs, Figure 6.3 compares two cases, i.e., pure DEP and thermally enhanced DEP. Red and blue marks depict instantaneous locations of NTs during the assembly process. At the initial stage, a series of NTs are distributed along the centerline with an equal spacing of 1 µm. Assuming the temperature gradient is constant in this system, the magnitude of the thermophoretic force remains unchanged.

Because dielectrophoresis is a near-field phenomenon, thermally induced particle motions are dominant at distant locations when DEP forces are small. Thus, the general velocities of the NTs are rather small. In a region within 2 µm distance of the electrodes, the thermophoretic force remains the same but the DEP force rises due to the increased electric field gradient in the proximity of electrodes. Therefore, the moving velocity of the NTs in the suspension significantly increases with decreasing spacing.
Figure 6.3 Sequential motion of CNTs undergoing pure DEP and thermally enhanced DEP. Red cross marks represent thermally enhanced DEP. Blue dots represent pure DEP.

The initial locations of N Ts experiencing pure DEP and thermally enhanced DEP overlap at \( t=0 \), corresponding to status 1. A gradual increase in the velocity of thermally enhanced DEP takes places at status 2, where red marks exhibit larger displacements than blue marks. As shown at status 3, the nearest red mark arrives at the desired assembly location across two opposing electrodes, while all blue marks
only make slight shifts from their original locations. At status 5, the second red mark arrives at the final location, while the blue mark is still approaching. The blue mark is observed to be eventually assembled at status 6. From these numerical simulation results, it is evident that CNTs at distant locations have a greater chance of being attracted by means of thermophoretic manipulation, despite the fact that the DEP forces are restricted in the neighborhood of the electrodes.

The purpose of thermophoresis enhanced DEP is the following: a) Long distance transport of nanomaterials can be realized through a controlled heating system, which compensates for drawbacks of conventional DEP, such as near-field effects and constraints on the geometry. b) Thermophoretic force can expedite the assembly process. c) With a hybrid DEP assembly approach, concentration is not as critical as before, because thermophoresis moves all CNTs to the desired electrodes if the electrodes are in the coldest region.

6.5 EXPERIMENTAL RESULTS

Experimental results based on this hybrid DEP method are obtained by inserting an electrical resistive heater into the nanoelectrode arrays. Nanoelectrode pairs for generating electric fields for DEP assembly were fabricated as described previously [63]. Each electrode consists of an 85 nm thick gold layer on a 15 nm chromium layer on the SiO$_2$ substrate. In Figure 6.4, two opposing electrodes of the electrode array are fabricated with a 200 nm width and a 200 nm gap. The resistive heater, which is composed of gold coils showing the overall resistance of 20 Ω, is placed 5 µm away from the nanoelectrode array. In our experiments, MWNTs (20-50 nm diameter, 1-5 µm length, arc-produced from MER Corp.) and N, N-Dimethylformamide (DMF) were used to make the CNT suspension. The suspension was ultrasonicated for six hours to ensure homogeneity and to keep the MWNT concentration stable. A concentration of 0.2 µg/ml was selected which corresponds to a single MWNT per 200 µm$^3$ solution. At this low concentration a relatively small number of nanotubes has the probability of being close to electrodes and, hence, makes purely DEP-induced assembly less likely. To justify this argument, a very low assembly yield is demonstrated at this concentration for conventional DEP experiments, i.e., experiments without a temperature gradient [68].
Figure 6.4 Fabricated nanoelectrode array with one electrical resistive heater. (The gap has the dimension of 200 nm)

Figure 6.5 illustrates the experimental steps using thermal enhancement. Prior to initiating resistive heating, a drop of MWNT suspension was deposited on the chip to cover the electrode array (Figure 6.5(a-b)). As soon as the 5 MHz AC electric field was applied, the heater was powered by applying a DC bias (Fig. 6.5(b)). After 100 s, the chip was removed from the probe station and blow-dried with a nitrogen gun. The assembly results were examined by SEM (Figure 6.5(c-d)). The primary mechanism is similar to particle deposition from a hot liquid onto a cold wall [198]: higher energy molecules in higher temperature regions induce a greater momentum to particles, resulting in a global particle migration towards the cooler side. When the resistive heater provides local heating in the suspension, the thermal forces induced by the temperature gradient move nanotubes toward the cooler electrodes where DEP comes into play, increasing the likelihood of nanotube deposition, even at low concentrations. These experimental findings are consistent with theoretical calculations in that thermally increasing the mobility of nanotubes increases their capture probability by the DEP force for successful assembly onto electrodes.
Figure 6.5 Schematic description of the DEP process with thermal assistance. (a) Nanoelectrodes are covered by a drop of nanotube suspension. (b) DEP assembly of nanotubes performed by applying an AC electric field to the nanoelectrodes in the temperature field generated by the resistive heater. (c-d) SEM pictures of individual MWNTs assembled by the thermally enhanced DEP method.

We performed several experiments using both conventional and thermally enhanced DEP approaches. As the induced thermal gradient was the only experimental parameter allowed to vary during experiments, the direct observation is that the thermally enhanced DEP results in more successful assembly results. The assembly yield based on sufficient repeatable experiments would be expected in the future study. Figure 6.6 shows the failure modes in this assembly step including imperfect nanotube, presence of multiple tubes, structure kink, and graphitic particles, which are commonly observed in the conventional DEP approach.
Implementing two heaters on the chip, thermophoresis can form a trap for assembling NTs onto the central electrode array. This technique is better characterized as thermal pushing or pulling where a liquid temperature gradient is created by two opposing heaters. Preliminary simulation results show that NTs have great possibilities to be confined in the center area, assisted by the intense DEP attraction.

Figure 6.7 Finite element model of two heater system. Arrow: temperature gradient. Contour: temperature distribution. Inset: Optical image of two heater system.
6.6 Summary

We have presented a simple but effective DEP technique enhanced by a temperature gradient that significantly improves mobility of CNTs in the suspension. The physics behind the responsible mechanisms of the thermally enhanced DEP approach have been investigated both theoretically and experimentally, and the selective manipulation and direct integration of individual MWNTs have been validated. The experimental observations of assembly results match well with a theoretical model used to calculate temperature field and simulate dynamic motions. This hybrid DEP method compensates for important deficiencies in conventional DEP and offers a new approach for the directed, high-yield self-assembly of micro/nano objects.
7 CONCLUSION AND OUTLOOK

Dielectrophoretic assembly of carbon nanotubes is a distributed control method driven by identification of optimum deposition parameters within the multi-variable process. Numerous sets of parameters have been explored through either pure experimental investigations or theoretical simulations. This thesis has designed and implemented several optimizing schemes for DEP assembly of CNTs into nano-devices with mass-production and high-precision. Dielectrophoresis is integrated into a series of techniques, such as the shaping electrode method, the floating-electrode approach and the thermophoresis-enhanced method. A number of key issues related to DEP assembly have been addressed, including: (1) the position and the orientation of the assembled 1-D nanostructures can be controlled; (2) cantilevered CNT nanostructures are reproducibly fabricated; (3) interference effects from the contact resistance during electrical measurement of the CNT-based devices are minimized. Both internal and external physical parameters have been examined to demonstrate their contribution to fulfilling controllable nano-patterns of CNTs and the specific positioning at large assembly scales that are vital to the eventual commercialization. The primary contributions of this thesis include:

- A finite element model has been developed through the analysis of electric field variation and the dynamic behavior of CNTs under DEP assembly, which offers insights into optimizing the DEP assembly method in terms of process metrics such as yield, precision and cycle time. The model is developed to be generally compatible and easily adoptable to diverse assembly systems.

- A hybrid approach modulating the nanoelectrode geometry while using other experimentally obtained parameters has been investigated for DEP assembly. The shaping electrode DEP method has been demonstrated to realize high-precision assembly of complex nanostructures.

- A floating-electrode DEP assembly method has been developed to realize simple, high-precision and controllable CNT assembly while preventing undesirable depositions. The significance of such assembled structures is further demonstrated by the ability to eliminate the contact resistance interference using four-point
electrical measurement. The results are critical to applications of MWNTs in electrical interconnects and nanoelectronic devices.

- Preliminary results of a novel, thermally enhanced DEP technique have been presented. It is found that the assembly speed and yield can be dramatically increased by inserting an external heating source into the fluid. This approach indicates that a second bottom-up approach joining with DEP assembly can bring desirable results and is feasible for integrating carbon nanotubes into nanoelectronic circuits and nanoelectromechanical systems (NEMS) with improved precision and yield.

Although significant progress has been made, future research work still needs to address the following topics: real-time monitoring, device development and three-dimensional systematic modeling for DEP assembly.

There is a clear trend towards wafer-level assembly of individual CNT-based devices using dielectrophoresis, with features of massively parallel device fabrication and reduction of waste of CNT materials. A way to enable this technology for large-scale industrial processes is the in situ monitoring of the DEP process by measuring the current, voltage and phase angle. In this way, a closed-loop system can be formed by giving feedback on the density and quality of CNTs deposited on the patterned electrodes. By tuning different operating parameters online, e.g., the electric field and field applying duration, an in situ monitoring system should provide valuable insights into the physical evolution of the DEP assembly process and reveal some of its intrinsic limitations. The real-time monitoring can create new optimizing methods for controlled nano-manufacturing, possibly making the production of the next generation CNT nanodevices practical and cost-effective.

In the area of device development, the assembled nanostructures using optimization techniques present competitive capabilities and offer potentials for future applications with high complexity and low power consumption. For example, a tunable dual-frequency carbon nanotube oscillator is proposed in [104], which is composed of a cantilever inner tube and a short outer tube. When the inner tube vibrates, the centrifugal force and the van der Waals force drive the outer tube to oscillate along the inner tube, which means that the oscillator can simultaneously output two frequencies. The combination of tunability and high-frequency operation
makes the oscillators promising for a variety of scientific and technological applications (Figure 7.1).

**Figure 7.1** Schematic diagrams for the tunable dual-frequency oscillators. (a) The inner tube is released with an initial deflection. (b) The outer shell extrudes from the inner shell under effect of centrifugal force, then the van der Waals forces gives rise to the retraction of the outer shell. (Images adapted from reference 104)

Other potential NEMS applications of the realized nanoarchitectures are data storage devices that employ a simple electromechanical switching rule, according to which the device is held together by a balance of three major forces: electrostatic, elastostatic and van der Waals forces (Figure 7.2) [108]. If individual cantilevered CNTs are assembled in the electrode array, single memory cells can be extended to three dimensional computing networks, in which two operating schemes shown in Figure 7.2, can be implemented simultaneously.

**Figure 7.2** (a) A three-terminal memory cell based on cantilever carbon nanotubes at conducting state. (b) A three-terminal memory cell based on two aligned cantilever carbon nanotubes at conducting state. (Images adapted from reference 108)

Another possible area of future research relates to developing a 3D model of dielectrophoretic assembly of nano-objects in a fluid. This thesis presents a 2D model based on the effective dipole moment method to study the on-chip shapes of electrodes and their influence on the DEP behavior. Due to their high dependence on
the electrode geometries, it may be challenging to accurately simulate the electric field distribution and the object trajectory when intricate 3-D nanoelectrodes are utilized in experiments. Moreover, the interaction between neighboring objects in the suspension must be considered when they are transported and deposited on the electrode array. In addition, the complex fluid dynamics characterizing the assembly process cannot be understood simply by adding a friction term to the equations of object motion. Instead, one must include an effective coupling of the immersed objects with the surrounding viscous fluid in the presence of an electric field. This would be of interest for modeling nonlinear fluids and in related to process conditions for commercial manufacturing.

Compared to conventional DEP methods, optimized DEP assembly approaches improves assembly throughput and efficiency and extends the range of DEP attraction. While the major interest here is manipulating CNTs via dielectrophoresis, these findings are also applicable for other materials such as graphene, bio-molecules, and metallic/semiconducting nanowires. It is thus possible that a number of research directions for advancing the contributions made within this thesis will be indicated, helping to create manufacturing processes attractive for industrial applications as the dimensions of components and modules downscale, and the market for multifunctional devices expands.
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