Dielectrophoresis-driven Assembly of Polymer Microbeads and Carbon Nanotubes Upon Fabricated Carbon Microelectrodes

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Tuo Zhou[1,2], Yu Lu[1], Sina Habibi Zad[3], Yeguang Zhou[1], Lixin Zhao[1], Lawrence Kulinsky[1]

[1] *Mechanical and Aerospace Engineering Department, University of California, Irvine*
[2] *Materials and Manufacturing Technology, University of California, Irvine*
[3] *Biomedical Engineering Department, University of California, Irvine*

Abstract

Microparticulates placed in non-uniform electric field experience dielectrophoretic forces that can be utilized for the guided assembly of microparts. The presented study discusses two types of such guided micro-assemblies. We observe the self-assembly of carbon nanotubes (CNTs) into the conductive bridges between microelectrodes along the field lines. These conductive bridges are later fixed in place by the layer of electrodeposited conductive polymer Polypyrrole (PPy). Additionally, we report on using positive dielectrophoresis (pDEP) to attract polymer microbeads to the windows opened in the SU-8 photoresist on top of the microelectrodes. The electric field is getting shielded by the photoresist and thus the beads are attracted only to the bare electrodes opened in the photoresist via standard lithographic process. Presented techniques open new possibilities for the guided assembly of micro-components for sensors, actuators, microelectromechanical systems (MEMs), as well as for micro- and nano-electronic devices.

Keywords: Micro-Assembly, Nano-manufacturing, Micro-manufacturing, Carbon Nanotubes, Interdigitated Electrode Arrays, Dielectrophoresis, Sensors, Microelectronics.

1. Introduction

Micro-assembly of the Microelectromechanical system (MEMS) or devices has gained a considerable attention over last few decades due to its potentials for a wide variety of applications, including sensors[1], energy storage [2], and Lab-on-Chip devices [3]. In order to maximize the efficiency of the devices and minimize their cost a rapid and scalable assembly technique is necessary. The traditional assembly techniques, such as robotic arm and pick- and- place techniques, are limited by significant time and cost associated with the serial steps of the processes [3],[4].

Alternatively, electrokinetic assembly [5], [6] can be a promising method of the guided microassembly. This technique can be employed to attract microparticulates, such as polystyrene beads suspended in aqueous medium to the microelectrodes via the dielectrophoretic (DEP) force in non-uniform electric field [7], [8]. The time-average DEP force (acting on homogenous spherical particle of radius R) is expressed by the following equation [9]:

$$F_{DEP} = 2\pi\epsilon_m R^3 Re[CM^*](\nabla E^2) \quad (1)$$

where ϵ_m is the permittivity of the medium, ∇E^2 is the gradient of the square of electric field, and the Re [CM*] is the real part of the Clausius-Mossotti factor which dependents on the effective polarizability of the particle and depends on complex permittivity of particles and the media [9] as expressed by the equation below:

$$CM^* = \frac{\varepsilon_p^* - \varepsilon_m^*}{\varepsilon_p^* + 2\varepsilon_m^*} \quad (2)$$

where the subscripts p and m stand for properties of the particles and media, respectively. The complex permittivity depends of the applied AC frequency of the signal and the change in the frequency of the applied potential can cause the change in the sign of the real part of CM factor (and the corresponding change in the sign of the dielectrophoretic force). The movement of particles in aqueous medium towards the electrodes is termed positive DEP(pDEP), while the repulsion of the particles from the electrodes is termed negative DEP (nDEP) [9].

We study the guided attraction of the particles to the pre-selected areas of the electrodes via pDEP where electrodes are covered by the layer of patterned photoresist that shields the electric field. Only the areas of the electrodes not covered by the resist will exert the attractive force on the microbeads in the surrounding solution.

In this work we demonstrate the successful guided attraction of 1um diameter beads to the 20 by 20 micron wide windows opened in SU-8 resist on top of carbon microelectrodes. We also demonstrate that electric field can be used to align carbon nanotubes along the field lines next to the electrodes.

If the electrodes are not covered by the patterned resist, the particuates will have the strongest attraction to the region of the highest gradient of the electric field – i.e. in the vicinity of the sharp corners and where the distance between the electrodes in the smallest. In this study we demonstrate how to use the dielectrophoretic attraction to assemble the bridges made out of carbon nanotubes (CNTs) in the region of the high gradient of the electric field. This study is the extension of the prior work where the bridges between the electrodes were formed with polymer microparticles [10]. Aligned CNT bridges between the microelectrodes have applications in the field of chemical and biological

sensors and in nanoelectronics [11-15].

2. Experimental Procedures

2.1. Fabrication of Interdigitated Electrode Arrays (IDEAs)

The carbon IDEAs of 40, 60, 90, and 120 micron wide with interelectrode gap distance of 40, 60, 90, and 120 microns (i.e. each design has interelectrode distance equal to the electrode width) and the length of each finger of 2000 microns (Figure 1 present schematics of the design of the electrode array) were fabricated by the conventional lithographic patterning of SU-8 2015 negative photoresist with subsequent pyrolysis of the SU-8 electrodes that converted that polymer precursor to glassy carbon [16],[17]. Heating and cooling rate as well as dwell temperature and time are of critical importance for pyrolysis process [18] and they are provided in Figure 2. Post-pyrolysis electrodes' height was measured to be 2.5 um. Before tests, the copper wires were soldered to the contact pads of the IDEAs with indium.

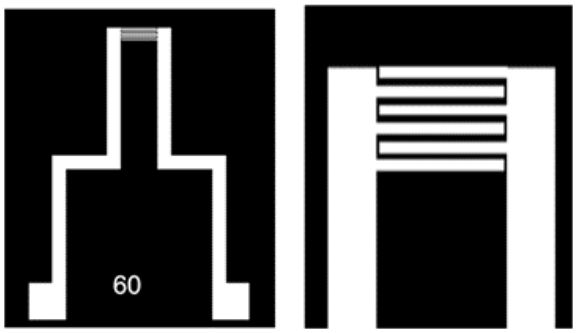

Figure 1. The schematics of electrodes design (left) and the magnified region of the interdigitated electrodes (right)

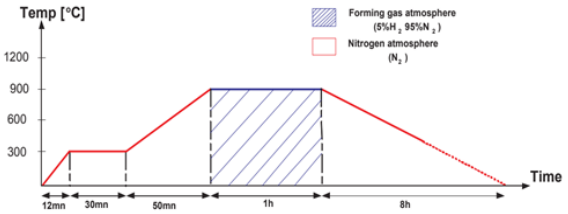

Figure 2. Pyrolysis steps for converting SU-8 precursor into carbon electrodes [18]

2.2. Formation of the patterned SU-8 resist layer above the electrodes

The SU-8 2002 resist was spun upon the wafer with the carbon IDEAs and subsequent lithography process was preformed utilizing Karl Suss MA56 Mask Aligner (Suss MicroTech, Germany) to produce 20 um x 20 um wells in the resist as demonstrated in Figure 3.

2.3. Experimental Setup

Carboxylated polystyrene microbeads 1 μm in diameter (Thermo Fisher Scientific., Grand Island, NY) were suspended in deionized (DI) water in ultrasonic bath for 30 minutes to homogenize the solution. A droplet of the solution with the microbeads was pipetted on top of the IDEAs, the IDEA chip was covered with a glass slide to decrease evaporation and facilitate observation of the movement of the beads with Eclipse LV-UDM Universal Design Microscope (Nikon Instruments Inc., Melville, NY). Electrical signals were supplied by the Function Generator DS345 (Stanford Research Systems, Sunnyvale, CA).

2.4. Carbon nanotube suspension

0.005 g of multi-walled carbon nanotubes (CNTs) (Sigma-Aldrich, St. Louis, MO) were weighed with ENTRIS64-1S Analytical Lab Balance (Sartorius GmbH, Goettingen, Germany) and mixed with the isopropyl alcohol (IPA) to make 10-mL solution. Large clusters of CNTs are precipitated after the tube with CNT solution is placed in the Branson 2800 Ultrasonic Cleaner bath (Emerson Electric Co., St. Louis, MO) for 24 hours followed by centrifugation in Eppendorf Centrifuge 5702 (Hauppauge, NY) at 1000 rpm for 10 minutes. The top supernatant with homogeneously distributed CNTs is pipetted into a separate tube, sonicated for 5 hours and used in the experiments described in this study.

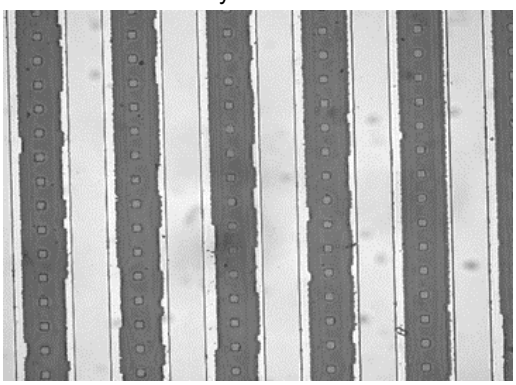

Figure 3. The carbon microelectrodes 120 micron wide with interelectrode gap of 120 microns and with SU-8 2002 resist deposited on top of electrodes (seen as translucent layer) and patterned to open 20 by 20 micron wells in the resist layer above the electrodes.

2.4. Deposition process for CNT bridges between microelectrodes

Carbon IDEAs with 60-micron wide electrodes and with inter-electrode distance of 60 microns are washed with DI water, acetone, and IPA sequentially and then dried with compressed air. Once the droplet of CNT solution is pipetted onto IDEA chip, the function generator is used to apply 10 V peak-to-peak (pp) bias with 0.1 MHz frequency and zero offset.

2.5 Polypyrrole deposition to secure attachment of CNT bridges

An electrodeposition of polypyrrole (PPy) is utilized to secure the attachment of CNT bridges between microelectrodes that form in the previous step. A mixed solution of 0.1M pyrrole monomers (Sigma-Aldrich, St. Louis, MO) and 0.1M NaDBS (sodium dodecyl-benzene-sulfonate) was prepared by dissolving 0.693 mL of pyrrole monometers and 3.48 of NaDBS in 100 mL of deionized water in an Erlenmeyer flask. The solution was stirred with the magnetic stirrer for 20 minutes at room temperature. Then several droplets of homogenized solution are placed on top of the deposited CNT bridges and the

function generator is used to apply AC signal with 0.6 Vpp and 1Hz frequency. After 30 seconds, a DC offset of 0.35 V is applied to initiate the PPy deposition as discussed previously [6]. After PPy deposition the electrodes are washed with DI water.

3. Results and Discussions

3.1. Determination of cross-over frequency for 1um diameter polystyrene beads

As we have discussed above, CM factor depend on the applied frequency. At low frequency the polystyrene beads experience positive DEP and are attracted to the electrodes, while at much higher frequency the CM factor becomes negative and the beads experience negative DEP (i.e. repelled from the electrodes). The frequency of transition from pDEP to nDEP is called the "cross-over frequency". By gradually increasing the applied frequency and observing the movement of the beads it was determined that the cross-over frequency for 1 um polystyrene beads in DI water was around 1.5MHz. At the applied frequencies below 1.5 MHz the beads experience positive DEP.

3.2. Entrapment of 1um beads into the wells

At the applied voltage of 3Vpp and applied frequency of 2.7 kHz the microbeads aggregated on top of the electrodes in the windows opened in the resist as Figure 4 demonstrates.

Simulation of the electric field distribution above the electrodes with and without the resist was performed using the multi-physics solver Comsol 5.3 (Comsol, Burlington, MA). Figure 5 presents the electric filed streamlines for 60 micron wide electrodes. It can be seen that in the case of 3 micron thick SU-8 resist (relative permittivity of 3) on top of the glassy carbon electrodes (relative permittivity of 30), the electric field lines above the resist have negligible vertical components and are directed towards the windows opened in the resist. These simulation results are supported by the experimental evidence that the beads on top of resist don't experience positive DEP, but in the vicinity of the windows opened in the resist the beads are agglomerated at the electrodes not covered by the resist.

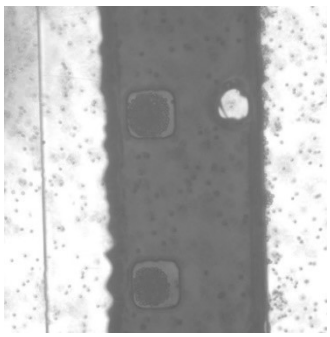

Figure 4. Guided assembly of 1 um beads to 20 by 20 micron windows opened in the resist on top of 60 micron wide electrodes.

3.3. Deposition of CNT bridges

While CNTs don't exhibit preferred orientation and appear randomly in the absence of external electric field [19], when the field is applied, the efficiency of alignment of CNTs depends on the frequency and the magnitude of the applied voltage under the influence of positive DEP and CNTs electrostatic interaction [20]. A range of applied voltages and frequencies was tried and it was concluded that bridges formed in the presence of strong positive DEP and that bridge formation was facilitated by higher applied voltages. The practical limitation was the presence of hydrolysis at low frequencies (where the positive DEP is the most pronounced), so the optimal tradeoff between the applied voltage and frequency was 10 V peak-to-peak with applied frequency of 0.1MHz and zero offset. Figure 6 presents the optical micrograph of the CNT bridges formed between 60 micron wide electrodes.

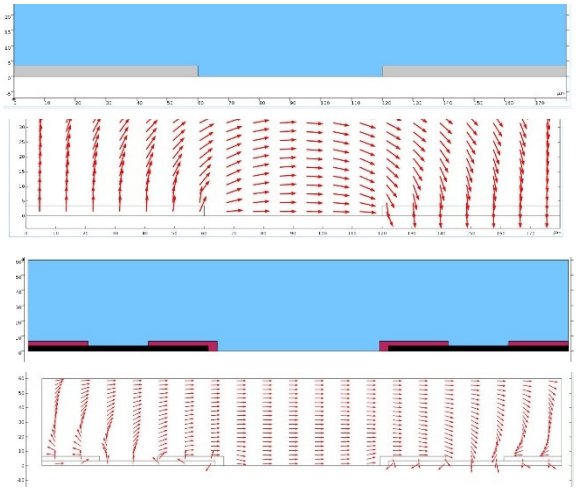

Figure 5. Streamlines of the electric field above the 60-micron wide electrodes without resist (top) and with 3 micron thick SU-8 resist that cover the electrodes leaving 20 micron wide window (bottom) demonstrate that the resist effectively blocks the electric field and that attraction of the beads will be directed towards the windows opened in the resist.

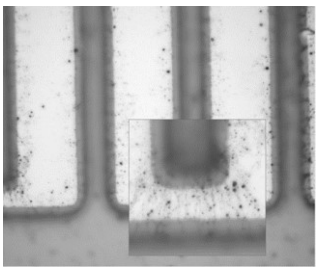

Figure 6. Carbon nanotubes aligned along the electric field lines under the influence of DEP forming bridges between 60 micron wide electrodes. The inset presents the magnified view of the CNT bridges.

3.4. Electrodeposition of Polypyrrole

After formation of CNT bridges, acetone and DI water were used to gently wash IDEAs and dry them with compressed air. The solution of PPy monomers and NaDBS was used to electrodeposit PPy for a period for 120 seconds using settings provided in the "Experimental Procedures" section. There was some darkening that could be visually observed on the electrodes and inter-electrode gap after PPy deposition. The IDEAs were dried for 24 hours at the room temperature after the electrodeposition of PPy.

3.5. Resistance measurement

The resistances of the IDEA were measured with digital INNOVA 3320 multimeter (Irvine, CA). CNT bridges were created by the sequential deposition of first, one drop with CNT suspension. After the sample was dried for 24 hours in the air, the resistance was measured. Then another drop of CNT solution was used for the bridge deposition and after the sample was dried, the resistance was measured again. It was repeated six times. Then polypyrrole was deposited on top of the bridges and resistivity was measured again after the sample was died. Figure 7 contains a plot of the measured resistances. It is clear from the plot that CNT bridges decrease the resistance between the electrodes. Increasing the number of CNTs above the electrode will decrease the resistance of the bridges, but after about three droplets of CNT solution, further adding of CNTs don't decrease resistance significantly. Data also demonstrate that PPy not only attaches the CNT bridges, but also reduce resistance further.

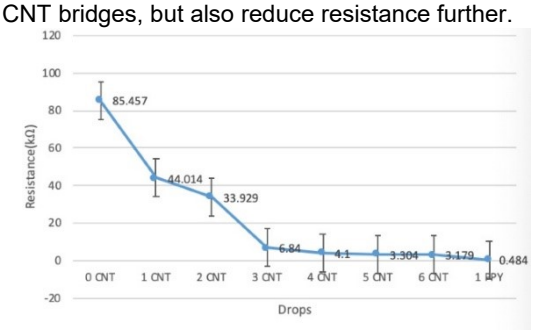

Figure 7. Resistance measurement of microelectrode systems after DEP guided deposition of CNT bridges with one to six drops of CNT suspension and for subsequent PPy deposition. Each resistance point represents the mean value of seven measurements. The error bars represent the standard deviation.

4. Conclusions

Presented study indicates the ways to use the dielectrophoretic forces to control electrokinetic assembly of polymer beads and carbon nanotubes. It was demonstrated that patterned SU-8 resist can be used as a template to guide the assembly of microparticulates to the specific locations on the electrodes. It was also demonstrated that CNT bridges between the electrodes can be assembled under the influence of the DEP force and then fixed in place by the subsequent PPy electrodeposition. The demonstrated toolbox of the electrokinetic assembly can find wide application for the fabrication of MEMS devices, sensors, and micro- and nano-electronic platforms.

Acknowledgements

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References

[1] S. Tadigadapa, et al., "Piezoelectric MEMS sensors: State-of-the-art and perspectives," *Meas. Sci. Technol.*, 2009.

[2] H. Liu, et al., "Piezoelectric MEMS energy harvester for low-frequency vibrations with wideband operation range and steadily increased output power," *J. Microelectromechanical Syst.*, 2011.

[3] M. B. Cohn *et al.*, "Microassembly technologies for MEMS," in *Materials and Device Characterization in Micromachining*, 2004.

[4] H. Van Brussel *et al.*, "Assembly of microsystems," *CIRP Ann. - Manuf. Technol.*, 2000.

[5] V. H. Perez-Gonzalez, et al., "PPyDEP: A new approach to microparticle manipulation employing polymer-based electrodes," *Lab Chip*, 2013.

[6] V. H. Perez-Gonzalez, et al., "A novel micro/nano fabrication process based on the combined use of dielectrophoresis, electroosmotic flow, and electrodeposition for surface patterning," *J. Micromechanics Microengineering*, vol. 25, no. 11, 2015.

[7] K. Kendall, "Electromechanics of particles," *Powder Technol.*, 2002.

[8] R. Antonio, ed. Electrokinetics and electrohydrodynamics in microsystems. Vol. 530. Springer Science & Business Media, 2011.

[9] R. Pethig, "Dielectrophoresis: Status of the theory, technology, and applications," *Biomicrofluidics*, 2010.

[10] C-I Cheng, et al., "The study of particle-particle interaction and assembly under the influence of dielectrophoretic force experienced between carbon microelectrodes", Proceedings of the World Congress of Micro- and NanoManufacturing, Portoroz, Slovenia, September 18-20 (2018)

[11] Ray H. Baughman, et al., "Carbon Nanotubes--the Route Toward Applications," in Science, Vol. 297, 2002.

[12] Junya Suehiro, et al., "Fabrication of a carbon nanotube-based gas sensor using dielectrophoresis and its application for ammonia detection by impedance spectroscopy," in IOPSCIENCE, 2003.

[13] Liu, et al., "Dielectrophoretic Manipulation of Nanomaterials and its Application to Micro/Nano-Sensors," in ResearchGate, Sensors and Actuators B: Chemical, 2008, pp. 664-670. 10.1016/j.snb.2008.03.032.

[14] Jingqi Li, et al., "Fabrication of carbon nanotube field effect transistors by AC dielectrophoresis method," in ScienceDirect, Vol. 42, Carbon. 2004, pp 2263-2267.

[15] Roberto Gambari, et al., "Applications to Cancer Research of "Lab-on-a-chip" Devices Based on Dielectrophoresis (DEP)," in SAGE Journals. 2003.

[16] M. J. Madou, *Fundamentals of Microfabrication*. 2018.

[17] Z. Tang, et al., "An optimized process for fabrication of high-aspect-ratio photoresist-derived carbon microelectrode array on silicon substrate," *Thin Solid Films*, 2010.

[18] B. Y. Park, et al., "Electrical properties and shrinkage of carbonized photoresist films and the implications for carbon microelectromechanical systems devices in conductive media. Journal of the Electrochemical Society, 152(12):136–143, 2005

[19] Yuegang Zhang, et al., "Electric-field-directed growth of aligned single-walled carbon nanotubes," in Applied Physics Letters, Vol. 79, Num. 19, 2001.

[20] Chen, et al., "Aligning single-wall carbon nanotubes with an alternating-current electric field," in Applied Physics Letters, Vol. 78, Num. 23: 3714-3716, 2001.