Fabrication of CNT Nanosensors by Combining Micro-Robotic Spotting and DEP Technologies

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Abstract—An automated Carbon Nanotubes (CNTs) microspotting system was developed for rapid and batch assembly of bulk multi-walled carbon nanotubes (MWNT) based nanosensors. By combining dielectrophoretic (DEP) and microspotting technique, MWNT bundles were successfully and repeatably manipulated between arrays of micro-fabricated electrodes. Preliminary experimental results showed that two different spotting methods were successful in forming CNTs between microelectrodes and the time required to form one CNT sensor was less than 1 second. This feasible batch manufacturable method will dramatically reduce production costs and production time of nano sensing devices and potentially enable fully automated assembly of CNT and other nanowire based devices.

Index Terms— **DEP manipulation, micro-robotic spotting, CNT sensors, nano manufacturing, nano batch fabrication.**

I. Introduction

Carbon nanotubes (CNTs) have been widely studied for their electrical (e.g., see [1]), mechanical (e.g., see [2]), and chemical properties since its discovery in 1991 by S. Iijima [3]. Owing to their minute dimensions and their tendency to cling together in nature, the connecting, aligning and isolating process of CNTs have been difficult for engineers and scientists world-wide. To manipulate these nano-sized tubes, atomic force microscopy (AFM) is typically used to manipulate each of them sequentially [4]. However, this is time-consuming and unrealistic when batch production is required. On the other hand, researchers have recently demonstrated different novel methods in carbon nanotube manipulation such as guided carbon nanotube growth [5][6], external forces [7][8], and polar molecular patterning [9]. Whereas the former technique grows organized carbon nanotube structures (guided/directed growth or assembly) by chemical-vapour deposition, the latter two methods are for pre-grown nanotubes. Currently, manipulation based on electric field generated force is becoming more promising, as it can be used to isolate, align and connect the metallic (electrically conductive) carbon nanotubes for nano-scale circuits or sensors congruently, while leaving the semi-conducting carbon nanotubes or impurities in a suspension [10]. K. Yamamoto et al. have pioneered the work in electric-field assisted manipulation of CNT bundles [11][12]. Our group has developed a systematic and time-efficient approach to engineer CNT based nanosensors [13][14].

In this paper, we will discuss our ongoing work to develop a more precise and efficient process for CNT batch manipulation by combining the dielectrophoretic (DEP) CNT manipulation and micro-robotic spotting technology. Preliminary experimental results have shown the validity of batch assembling of arrays of CNT sensors by using an automated CNT micro-spotting/injection system. The methodology of the manipulation process and architecture of the automated CNT micro spotting/injection system will be described in this paper. Experimentally, the main problem in developing such a system is the elimination of the adhesion force between the CNT-dilution and spotting probe tip, and the alignment of the probe tip to the sensor microelectrodes. The solutions to overcome these problems are also presented in this paper.

II. Automated CNT Microspotting System

A computer-controlled CNT microspotting system was developed for performing the dielectrophoretic CNT manipulation automatically. The theoretical background and basic results of non-automated DEP CNT manipulation was reported previously in our work [15]. This new developing automated system allows the CNT/ethanol solution to be ejected to the microelectrodes precisely, and the volume of CNT/ethanol droplet could also be well controlled, resulting in a high precision method to batch assemble CNT devices. In short, in order to build the functional micro-robotic system to assembly CNT sensors, we have developed 3 different technologies: 1) DEP CNT manipulation, 2) shaping of micro capillary probes to minimize CNT dilution droplet, and 3) fluid ejection through our fabricated micro probes, and positioning of the probe tips to the sensor electrodes through a micro-robotic station.

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A. *DEP Manipulation of CNTs*

As mentioned earlier, our group has already done significant studies on the DEP manipulation of CNTs. We will only briefly describe the process here. For details of the DEP manipulation process [14][15] can be referenced. Basically, the carbon nanotubes were dispersed inside a liquid medium (e.g., ethanol), and then drops of the liquid medium were placed between a pair of conduction electrodes with gaps ranging from 2 to 5μm between them. Then an AC voltage at specified frequency and amplitude (16Vpp, 1MHz) were applied to the electrodes, and CNT bundles would then form between the electrodes as the liquid medium evaporated. Dielectrophoresis refers to the force exerted on a polarized particle in a non-uniform electric field, and can be written as

$$\boldsymbol{F}_{\boldsymbol{DEP}}(t) = (\boldsymbol{m}(t)\cdot\nabla)\boldsymbol{E}(t) \tag{1}$$

where E is the electric field, m is the induced dipole moment of a CNT. Since the CNTs were first mixed in a liquid medium, the total force acting on a MWNT is the sum of a number of independent forces. With negligible gravitational force, the three main force components are the DEP force, the viscous force and the electro thermal force. Normally, for small particles with volumes similar in size as a CNT, the thermal effects can dominate. However, we have shown that the high polarizability of CNTs make the DEP force large enough to produce the deterministic movements close to the electrode gap. Thus, the depositions between adjacent electrode edges are dominated by DEP.

B. *Fabrication of Nanometric Probes*

Tip profile of a probe directly affects the size of a micro liquid droplet spotted on the surface of a substrate. Smaller probe tip diameter allows a micro-injection to eject smaller size droplets, and consequently, allows the CNT dilution or chemical liquid spot size to be smaller on a chip. Capillary probes (TSP0002150 with inner diameter of 2 μm and outer diameter of 126 μm, Polymicro Technologies) were fabricated by our novel chemical etching process, which employed glass tubing as a sacrificial barrier, to control and sharpen the probe into different tip profiles as shown in Fig. 1. Details of the fabrication process developed by our group can be found in [16].

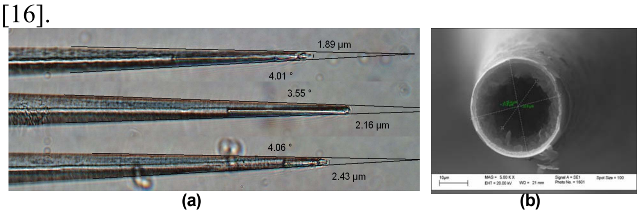

Fig. 1. (a) Microscopic image showing different capillary probe tips were sharpen by our chemical etching process. (b) SEM image showing a sharp tip with the inner diameter.

C. *Micro-Robotic Spotting System*

A micro-robotic station with a computer controllable X-Y-Z micromanipulator to manipulate the micro capillary probe tips to appropriate positions on a sensor chip, and a computer controllable hydraulic pump system to inject CNT solution through the capillary probes was integrated as shown in Fig. 2. Essentially, a microchip with arrays of microelectrodes can be placed on the sample stage with its movement controlled by the X-Y stage. An AC voltage can then be applied between the microelectrodes to initiate the CNT DEP manipulation process as mentioned before as soon as a micro-droplet is placed between a pair of electrodes by the micro-injection capillary probes. However, to inject the CNT/ethanol solution spots precisely to the microelectrodes is not a trivial task. Several injection experiments were conducted to study the micro-droplet formation phenomenon and will be presented in the following sections.

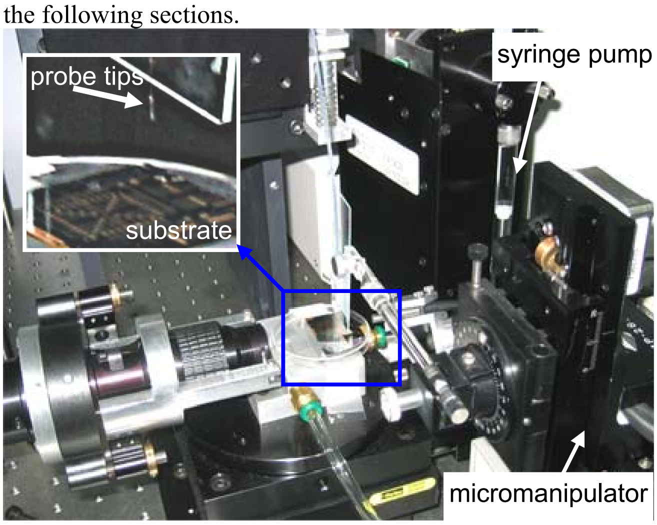

Fig. 2. Microspotting system with syringe pump and micromanipulator.

III. CNT Nanosensors Fabrication

CNT dilution injection is challenging because of the difficulties of ejecting very small CNT/ethanol solution to particular positions automatically and precisely. It is not only required to overcome the strong adhesion force (between probe tip and fluid), but to eject the CNT dilution spot size as small as possible, so that the droplet will only cover one pair of microelectrodes is also a problem. The following sections show our experimental results involving: 1) difficulties of the microspotting process, 2) position control of the X-Y-Z micromanipulator, 3) experimental result of different microspotting methods, and 4) experimental result of batch CNT formation.

A. *Microspotting Experiment*

Preliminary experiments were conducted to understand the microspotting process. Before the spotting experiment, a silicon substrate was placed on a stage. A fabricated capillary probe was mounted on a programmable X-Y-Z micromanipulator (MP285, Shutter Instrument Company), which was used to move the probe to the desired position of the substrate. A syringe pump (V6 syringe drive modules, Kloehn Limited) was connected to the capillary probe and was used to drive the probe to eject the fluid droplets to the substrate. It was successfully demonstrated that ultra small fluid droplets could be spotted as shown in Fig. 3. The droplet size could be much smaller by using our fabricated probe then the original capillary tubes from the vendor.

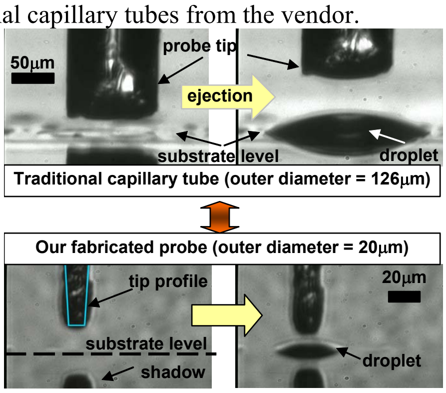

Fig. 3. Microscopic images [side view] showing the comparison of droplet sizes ejected from different outer diameter probe tips.

It was found that the adhesion force between the outlet of the capillary probe and the fluid droplet was significant during the experiment, i.e., fluid may not able to be ejected as shown in Fig. 4. Fluid droplet typically came out from the outlet of the capillary probe but stuck on the capillary probe side wall until the droplet became very large.

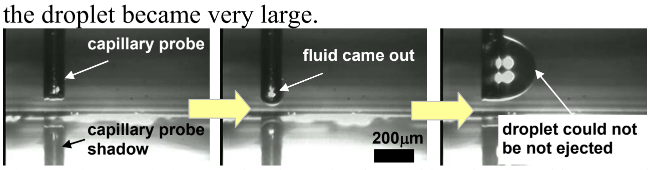

Fig. 4. Microscopic images showing a droplet could not be ejected because of the large adhesion force.

Fortunately, the effect of adhesion force could be eliminated by different methods such as reducing the gap distance between the probe tip and the substrate, i.e., moving the probe tip very close to the substrate and allow the liquid droplet to touch the substrate (contact method), or increasing the injection pressure (injection method). However, since the required pressure gradient to induce a fluid flow in a microchannel is large, the injection process is less practical to implement. Hence, we studied the effect of probe-tip-to-substrate distance in forming solution spots on the substrate (as shown in Fig. 5). In essence, we use micro-robotics technology to control the distance of a probe tip to a substrate such that a fluid droplet coming out of a probe tip could come to contact with the substrate and form a solution spot on the substrate, without the probe tip actually touching the substrate. Note that the formation of the droplet at the probe tip can be realized by either applying a large hydraulic pressure or simply by capillary force inside the microchannel of the fiber probe.

Detailed analysis of a typical single spotting process using this *droplet contact method* is shown in Fig. 6. The probe tip was moved to 30μm above the substrate (see Fig. 6a). A pressure was applied to eject the fluid, but the significantly large surface energy of the fluid caused it to form a concave droplet at the tip (see Fig. 6b). When the fluid touched the substrate, the tip-fluid interface and fluid-substrate interface were formed (see Fig. 6c). If the probe tip remained stationary and the volume of the droplet remained constant, the interfaces came to an equilibrium state (see Fig. 6d). Afterward, the probe tip was moved upward, the fluid interface was broken at the middle because the surface energy is not strong enough to keep the configuration, i.e., the fluid surface force was weaker than the fluid-substrate interfacial force (see Fig. 6e). Finally a droplet was left on the substrate (See Fig. 6f).

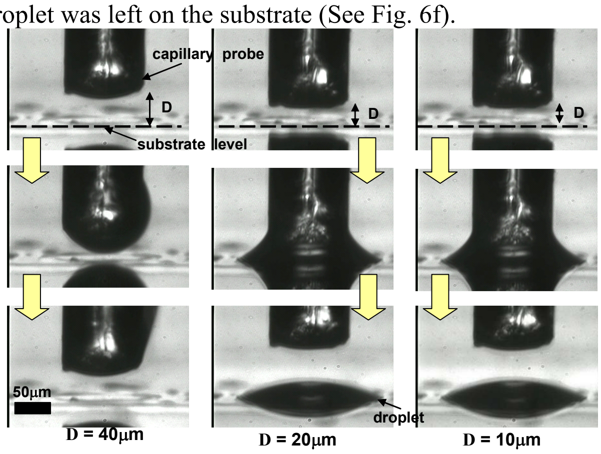

Fig. 5. Microscopic images showing a droplet can be ejected by reducing the initial gap distance between the probe tip and substrate. The images in each column represent different trials of initial gap distance. The images in the first row show the initial position of capillary probe. The images in the second row showing fluid was ejected from the probe. The images in the third row showing the fluid droplet could be ejected when D = 20μm and D = 10μm.

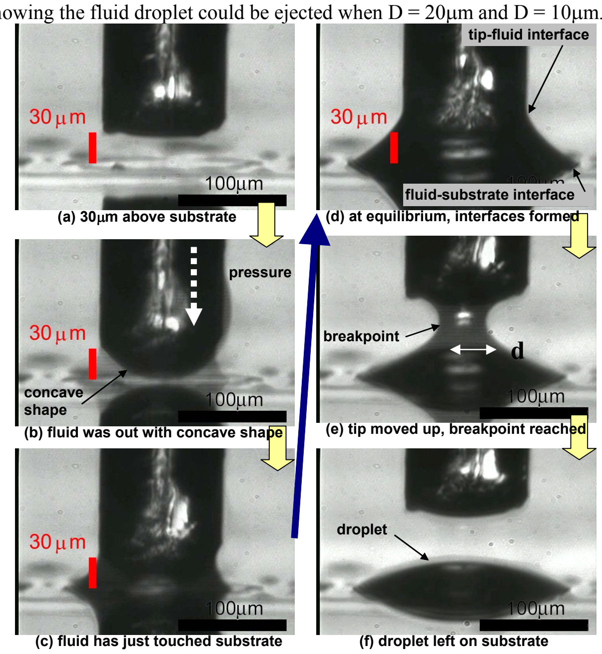

Fig. 6. Microscopic images showing a typical single spotting process.

The force required to maintain the equilibrium of the fluid between the tip and the substrate can be characterized by the following equation [17],

$$F = 2\pi r^2 \gamma_l \cos\theta_c / z \qquad (2)$$

where r is the radius of the fluid droplet, γ_l is the liquid-air interfacial tension, θ_c is the contact angle and z is separation between two solid surfaces. The contact angle, which is defined from the Young's equation [17], is the resultant of liquid-air, solid-air, and liquid-solid interfacial tensions as shown in Fig. 7a (one can also think of F as the capillary force acting between the probe tip and the substrate). Micro spotting experiments of ethanol were conducted for various initial tip-substrate separations, and the contact angles were measured from the microscopic images at breakpoint (see Fig. 6e). The contact angles were defined as shown in Fig. 7b and were from 23.2° to 38°. Based on equation (2), the applied forces were estimated consistently in between 0.50 μN to 0.63 μN as shown in Fig. 8. On the other hand, the work of cohesion, which is defined as the work required to separate two fluidic surfaces per unit area (or, conversely, the work required to keep two fluidic surfaces together) is given by the following equation [18]:

$$W_c = 2\gamma_l \qquad (3)$$

Note here that this *work per unit area* can also be expressed as a *surface force per unit length* (by unit equivalency). Hence, to estimate the surface force of an ethanol droplet, equation (3) can be used. With its surface tension (γ_l) of ~2.23 mN/m at 20°C, the surface cohesion force (F_c) of an ethanol droplet at breakpoint can be estimated by multiplying W_c with the cross-sectional diameter d (as defined in Fig. 6e). As shown in Fig. 8, the applied force (estimated by calculating the capillary force F) to separate a droplet from the probe tip to the substrate was consistently greater than the surface cohesion force of the ethanol droplet, which makes sense because F must be greater than F_c for a droplet to be separated from the probe to the substrate. By understanding the governing physical mechanisms during the spotting process, we can later optimize the vertical travel distance of a micro-robotic manipulator in order to minimize production time of large arrays of CNT sensors.

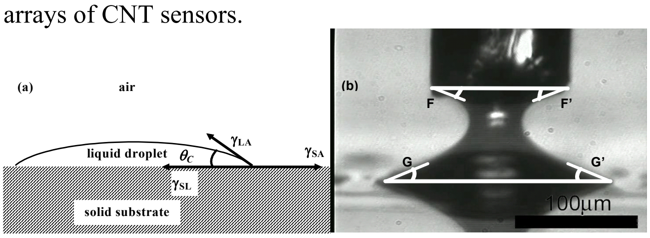

Fig. 7. (a) Contact angle at a liquid-solid interface of Young's equation. (b) Microscopic image showing the definition of contact angles of a droplet right before it "breaks".

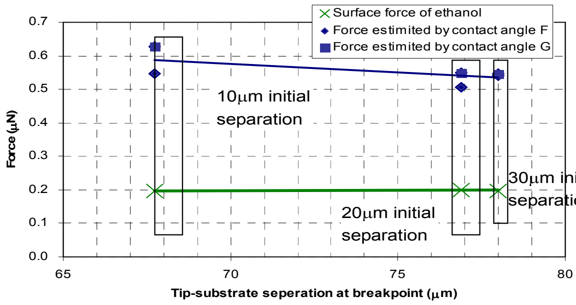

Fig. 8. Applied force on a droplet to separate it was estimated based on measured contact angle. The applied forces were consistently larger than the surface cohesion force of ethanol.

B. *Position Control of Micromanipulator*

Since sensor chips with arrays of microelectrodes can be fabricated by a standard microlithographic technique, a CIF-mask computer file can be generated by appropriate commercial MEMS or IC design software packages to assign coordinates to a micro-robot for CNT-solution spotting. For our work, we used MEMSPro™ and added a custom "CNT layer" on the software to record different positions of microelectrode gaps onto a CIF-mask data file. This file is then imported to our automated CNT microspotting system to command the motions of the micro-robotic manipulator and stage. For example, all positions of the center of the gaps between pairs of electrodes can be obtained and stored in array of X-Y coordinate system. Then, an arbitrary reference frame can be chosen to move the micro-manipulator. Currently, we choose the upper-left microelectrode as the initial reference position, the next position is obtained by finding the nearest neighbor from remaining microelectrode pairs (sorting principle) as shown in Fig. 9.

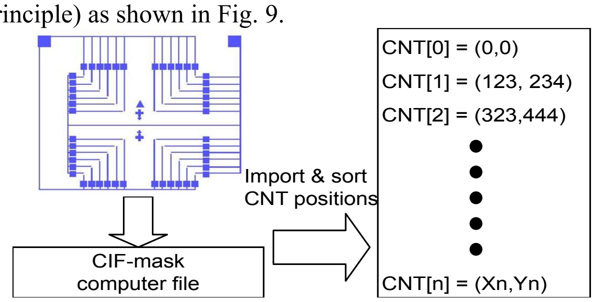

Fig. 9. Illustration of CNT position assignment.

As mentioned earlier, the probe is attached to a programmable X-Y-Z micromanipulator (MP285, Shutter Instrument Company), and a CCD camera is connected with the microscope to locate the initial position of the array of microelectrodes through a computer screen. The probe tip is required to align to the initial (upper-left) microelectrode so that it and the electrode could be observed under the microscope as shown in Fig. 10. Our group is also currently working on automating this initial reference-site finding.

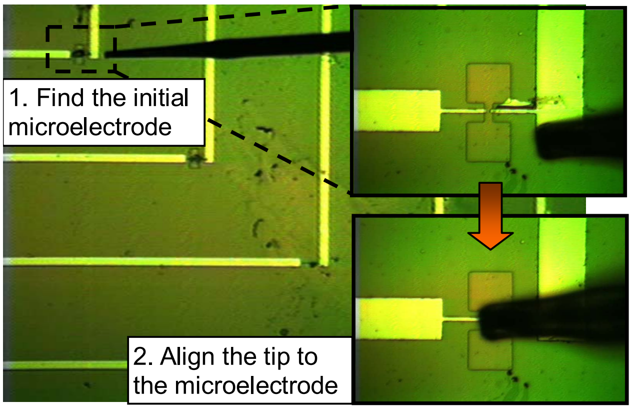

Fig. 10. Probe tip must align to the initial microelectrode.

After the initial position was determined, the spotting process began. The probe tip was automatically moved to positions which were above each microelectrode, then it was moved downwards to the substrate, and the syringe pump ejected the CNT/ethanol solution from the probe to the substrate. Finally, the CNT/ethanol spots were dropped in between each pair of microelectrodes automatically as shown in Fig. 11. We have found that the time required for manipulating CNTs to form between each sensor-electrode-pair by using this automated microspotting system is less than 1 second.

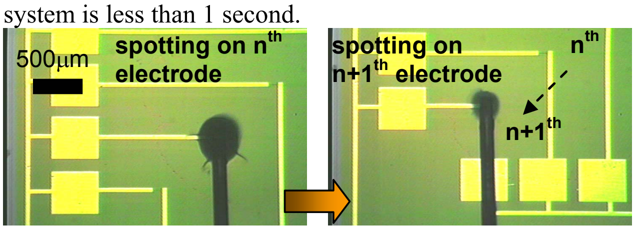

Fig. 11. Probe tip moved and dropped CNT/ethanol solution on different microelectrodes.

C. CNT/Ethanol Solution Spotting Experiment

Experiments were conducted by using our fabricated probe with 100 μm I.D. and ~125 μm O.D. In the experiment, an AC voltage (16 Vpp, 1 MHz) was applied to the sensor chips (with array of 24 pairs of fabricated micro electrodes in each chip) to DEP manipulate CNTs across the micro electrodes. The probe was tilted in order to reduce damaging effects on the probe as it hits the substrate. Two different spotting methods were conducted to study the performance of the micro-robotic spotting system: 1) *injection method* -- spotting using a syringe pump to induce enough hydraulic pressure (24 drops), 2) *droplet contact method* - spotting by allowing a droplet to come in contact with the substrate as described earlier. However, for the contact method, two scenarios were tested: a) 24 drops were spotted on the sensor chip, and b) 4 drops were spotted on the sensor chip. The sequence of the micro-robot movement in spotting the sensor chip is shown in shown in Fig. 12.

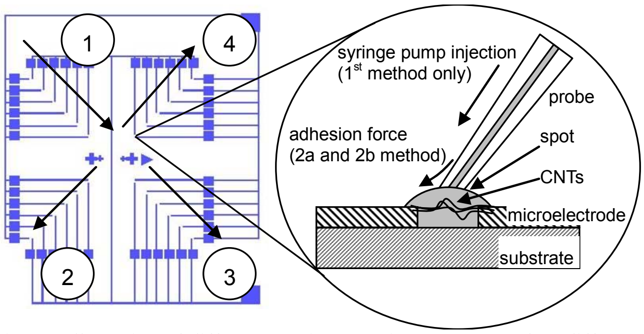

Fig. 12. Illustration of different spotting experiments. 1-4 are four different regions on the sensor chips. Each region consists of 6 pairs of micro electrodes. Arrows are the sequences of spotting 24 spots (the 1st and 2a method). The 2b method spotted only 1 spot on each region.

Bundled CNTs were manipulated successfully across the micro electrodes by using all three different methods mentioned above. It was observed that the amount of CNTs formation was affected by the spot size, so spot size and concentration of the CNT/ethanol solution must be controlled precisely. By using the syringe pump injection method, the spot size cannot be very small (i.e., >1000μm), and the solution spots may cover more than one pair of micro electrodes. On the contrary, the spot size can be very small (~40 μm) by using the *droplet contact method* (2a method and 2b method), but it usually spots relatively big spots at the initial few spots (~300 μm), causing larger amount of CNTs formation. This is the reason why methods 2a and 2b were compared, i.e., the effects of successive spotting using the *droplet contact method* and thus be investigated.

D. Experimental Results of CNT Formation

After applying the DEP voltage and spotting the CNT/ethanol solution on the defined positions of the chips by any of the three spotting scenarios mentioned before, it was observed that the ethanol is evaporated away very quickly, leaving the CNTs to reside between the gaps of the microelectrodes. The corresponding connections of bundled CNTs for a representative pair of microelectrodes using the three different spotting conditions are shown in Fig. 13. We have observed that the CNT formations by using three different spotting methods are similar and the CNTs were successfully connected between the microelectrodes. In order to confirm the linkage of bundled CNTs across two microelectrodes, the room temperature resistance corresponding to each pair of microelectrodes was measured. The CNT connection process was deemed successful between two microelectrodes when the room temperature resistance measured became several kΩ to several thousand kΩ. The chips were also eventually checked using a scanning electron microscope (SEM) to validate the CNT connections between the electrodes. Since the conductivity of CNTs depend on their lattice geometries during their growth process, the conductivities of individual CNTs cannot be well controlled, which results in the variation of conductivities in individual CNTs. During the DEP process to form CNT bundles across microelectrodes, the CNTs were randomly connected between microelectrodes. Therefore, it is logical that different CNT samples exhibited different conductivities. The room temperature resistances of different sensors of the chips by using different spotting methods are shown in Fig. 14. In addition, plots of statistical data for different spotting experiments were generated (see Fig. 15), which shows the maximum, minimum, average and standard deviation (S. D.) among the measured resistances on each spotting experiment.

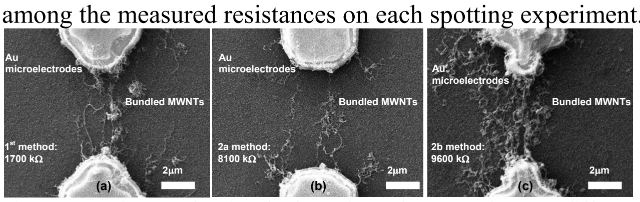

Fig. 13. SEM images showing the formations of MWNTs between different pairs of Au microelectrodes by different conditions. (a) Spotting using syringe pump (24 drops), (b) spotting using contact method (24 drops), and (c) spotting using contact method (4 drops).

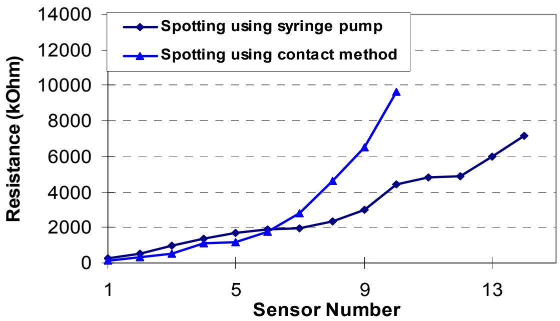

Fig. 14. Statistical data of measured resistances on different sensors of different chips by using two different spotting methods. (The resistance of the corresponding sensor is sorted in ascending order.)

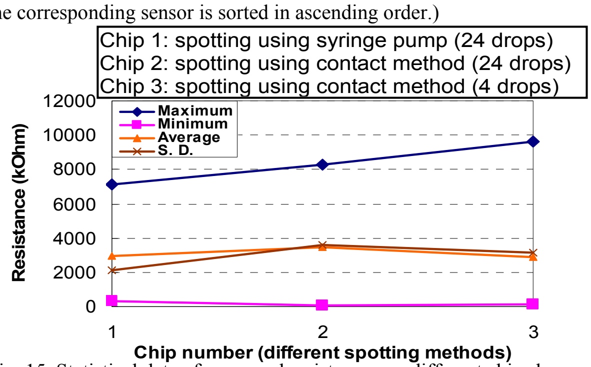

Fig. 15. Statistical data of measured resistances on different chips by using three different spotting conditions.

IV. Conclusion

An automated microspotting system to batch fabricate nanosensors with CNT sensing elements based on dielectrophoretic manipulation was presented. We have demonstrated two different spotting methods to form the CNTs between the microelectrodes successfully and the time required to manipulate one CNT sensor is less than 1 second. This is a promising indication that DEP manipulation process combined with the automated microspotting system is a feasible technology to batch assemble CNT functional devices in a fast and precise manner.

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