Towards Batch Fabrication of Carbon Nanotube Sensors by Combining Microinjection and Dielectrophoretic Manipulation

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***Abstract* – We present the preliminary design and test results of a novel automated Carbon Nanotube (CNT) microinjection system for batch fabrication of a bulk multi-walled carbon nanotubes (MWNT) based sensors. This project will eventually develop an automated system to rapidly and precisely execute the AC electrophoretic manipulation of MWNT bundles on substrates that are used to fabricate nano-sensors. We have already shown that, using dielectrophoretic manipulation, CNTs were successfully and repeatably manipulated between micro-fabricated electrodes. The CNT devices were demonstrated to potentially serve as novel thermal sensors with low power consumption (~μW) and electronic circuit response of about 100 kHz in constant current mode operation. Besides, preliminary microinjection experiments were conducted which demonstrated the possibility of the automated microinjection of solution with spot size of ~200μm. Based on these experimental evidences, a feasible batch fabrication method for functional CNT sensors by using an automated injection system is under development. The system will ultimately reduce fabrication accuracy and time of nano sensing devices and potentially enable fully automated assembly of CNT and other nano-wire based devices.**

Index Terms - AC electrophoretic manipulation, carbon nanotube, CNT sensors, microinjection, nano batch fabrication.

I. INTRODUCTION

Carbon nanotubes, has been widely studied for its electrical, mechanical, and chemical properties since its discovery. In order to build a CNT based device, fast and batch techniques to manipulate the CNT has to be developed. Currently, the widely accepted technique for manipulating nanowires and entities is by atomic force microscopy [1]. However, this pick-and-place technique is time consuming, which is unrealistic for batch fabrication of nano devices. On the other hand, past demonstrations by K. Yamamoto et al. showed that carbon nanotube can be manipulated by AC and DC electric field [2][3], and a recent report from L. A. Nagahara et al. also demonstrated the individual single-walled carbon nanotube (SWNT) manipulation using nano-electrodes by AC bias voltage [4]. By using a similar technique (i.e., AC electrophoresis), we have successfully manipulated bundled carbon nanotubes to form resistive elements between Au microelectrodes for sensing and electronic circuits efficiently. However, in our prior work, we found that the yield of the batch assembly of the CNT devices cannot be 100% as the volume of each drop of the CNT/ethanol solution during the CNT manipulation process cannot be controlled precisely. Therefore, in order to improve the yield, a precise and automated CNT injection system is under development in our group. This paper first reports the technique to form bundled MWNT resistive element between Au electrodes. Accordingly, AC electrophoresis makes the batch fabrication of nano devices using nanotubes as components feasible. We have proven that carbon nanotube devices built by this method are capable of performing very low power thermal sensing (i.e., ~1000 times lower than conventional MEMS polysilicon based thermal sensors) and can be fabricated in a relatively fast and efficient manner [5]. The detailed process to manipulate nanotubes using AC electrophoresis and the experimental results from using the carbon nanotube bundles as thermal sensing elements will first be presented. In addition, we will report our development of the automated CNT microinjection system, which requires our team to overcome some engineering problems such as eliminating the adhesion force between the fluid and the probe tip that is eventually used to dispense CNT solutions, and the precise alignment of the probe tip to the sensors microelectrodes that is used to apply dielectrophoretic force. The preliminary microinjection experimental results will be presented, which shows that fluid droplets of ~200um diameter can be ejected from the capillary tubes with inner diameter of ~10**μm** to desired positions on a substrate precisely. Moreover, the volume of fluid droplet can be consistently controlled, which is a factor affecting the yield of the batch assembly of CNT devices.

II. AC BATCH ELECTROPHORETIC MANIPULATION OF CNT

In our CNT dielectrophoretic manipulation experiments, the carbon nanotubes were dispersed inside a liquid medium (e.g., ethanol), therefore other forces (e.g., viscous force), other than the dielectrophoretic forces are also imparted on the carbon nanotubes during the manipulation process. In order to understand the physical phenomenon during the dielectrophoretic manipulation, we have previously conducted the simulations on the effect of different microelectrode geometries on carbon nanotube alignments and the results can be found in [6].

A. Experimental Details and Results

Based on the physical phenomenon of AC electrophoresis [6], we have successfully manipulated the bundled CNT on

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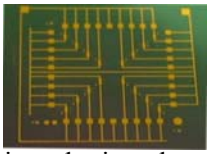
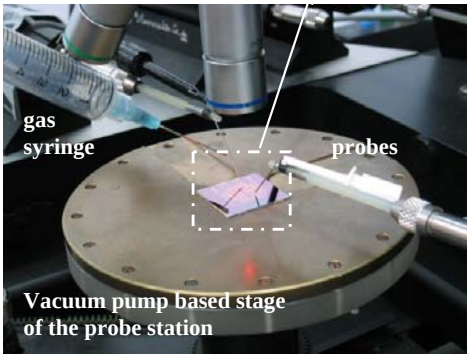
fabricated microelectrodes. The experimental process flow for the CNT manipulation can be divided into three parts: fabrication of microelectrodes, sample preparation and experimental testing (see Fig. 1).

MWNT powder



Fabricated microelectrodes on a silicon substrate



Excitation of the circuit by AC voltage source and transferring of the MWNT/ethanol suspension to the substrate

Fig. 1. Experimental setup for CNT manipulation using AC electrophoresis.

The Au microelectrodes were fabricated on glass or Si/SiO_2 substrates by a standard technique as described in [7]. Bundled MWNTs (which were ordered commercially from [8]) were prepared by a sonication treatment. The axial dimension and the diameter of the MWNTs were 1 – 10μm and 10 – 30nm, respectively. In order to form stable colloidal suspension of MWNTs and minimize the degree of aggregation, 50mg of the sample was ultrasonically dispersed in 500mL ethanol solution and the resulting solution was diluted to 0.01mg/mL for later usage.

During the CNT manipulation, a substrate with Au microelectrodes was placed on the stage (with a vacuum pump) of a micromanipulator station, which allowed the probing of microelectrodes by microprobes. Au microelectrodes were then excited by an AC voltage source with typically of 16 V peak-to-peak with frequency of 1 MHz. Approximately 10μL of the MWNTs/ethanol solution was transferred to the substrate by a 6mL syringe. The ethanol was evaporated away leaving the MWNTs to reside between the gaps of the microelectrodes. We have observed from the experimental results that bundled MWNTs was attracted towards the Au microelectrodes under non-uniform electric field and connected across the microelectrodes. A representative SEM image showing the bridging of MWNTs across the Au microelectrodes is shown in Fig. 2.

The formation of MWNTs linkages can be further confirmed by testing the connectivity between the pair of microelectrodes. For instance, room temperature resistances between the microelectrodes were measured and the two probe room temperature resistances of the samples typically range from several kΩ to several hundred kΩ, which suggested the connection had been formed between the two microelectrodes.

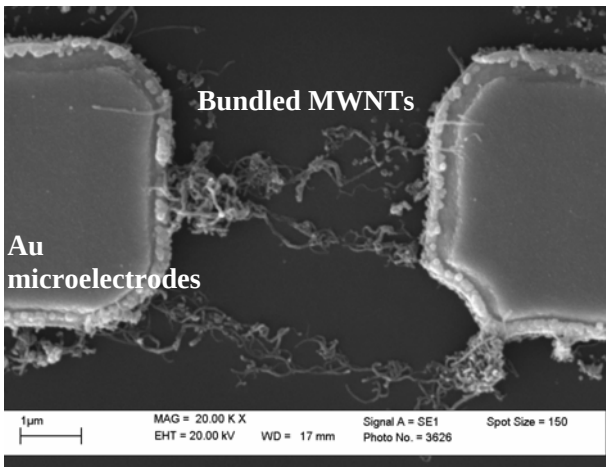
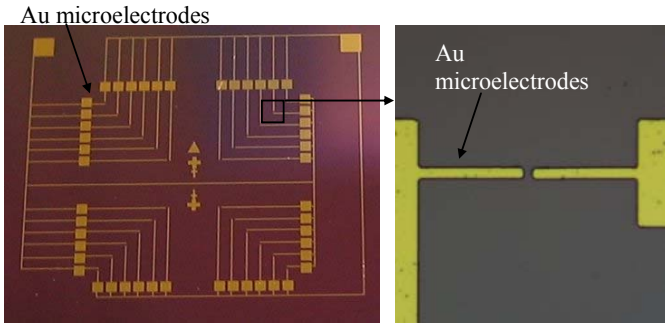


Fig. 2. Scanning electron microscopic (SEM) image showing the MWNT connections between Au microelectrodes.



(a) (b)

Fig. 3. (a) Photograph of the fabricated arrays of Au microelectrodes on a substrate. (b) Optical image showing a pair of Au microelectrodes before CNT manipulation.

As mentioned in the pervious section, AC electrophoretic manipulation is different from those traditional pick-and-place manipulations (e.g., AFM manipulation) which can only assemble CNT devices one at a time. Instead, AC electrophoretic manipulation is a parallel assembly process where batch assembly of CNT devices is theoretically possible when the electrical potential is applied to an array of microelectrodes which are connected electrically together. To prove the validity of batch assembling by AC electrophoresis, we have implemented the experimental procedures mentioned and extended to an array of Au microelectrodes which are electrically connected together on a substrate (see Fig. 3). By using the same experimental parameters presented before, we have successfully manipulated the CNT bundles on most of the Au microelectrodes by AC electrophoresis in a single-run fashion. The connections of bundled CNT for different pairs of microelectrodes on a substrate after addition of one drop of

MWNTs/ethanol solution (~ 10μL) were shown in Fig. 4. In order to confirm the linkage of bundled CNT 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 hundred kΩ. Several chips were then checked using SEM images to validate the CNT connections between the electrodes.

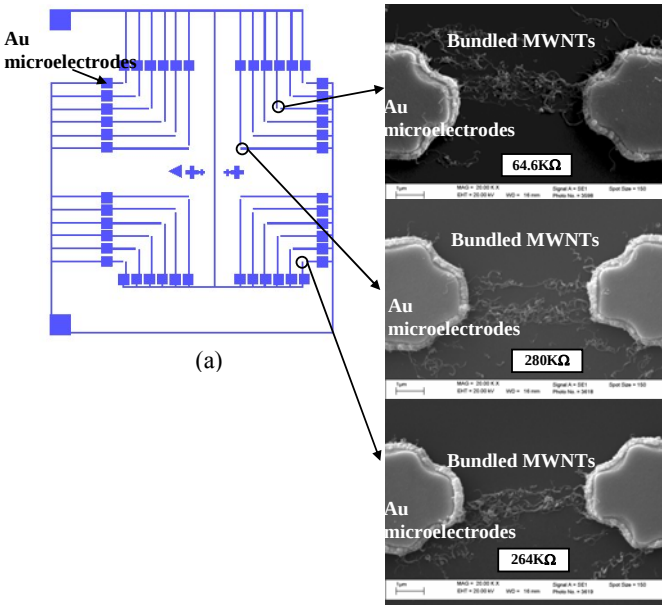


Fig. 4. (a) Drawing of the design for the chip with arrays of Au microelectrodes. (b) Scanning electron microscopic (SEM) images showing the formations of MWNTs between different pairs of Au microelectrodes.

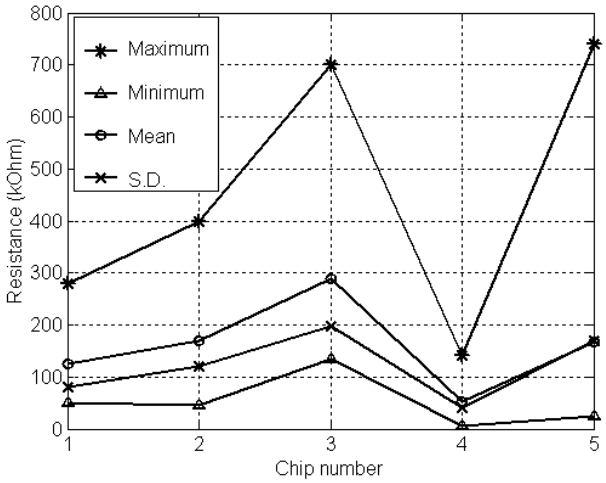


Fig. 5. Plots of statistical data of measured resistances between the Au microelectrodes on different samples.

To validate the consistency of the batch assembly of CNT devices, repeated experiments for AC electrophoretic batch manipulation of CNT between the arrays of Au microelectrodes were performed and plots of statistical data for different experiments were generated (see Fig. 5), which shows the maximum, minimum, average and standard deviation (S. D.) among the measured resistances on each sample. From the experimental results, we have observed that the range of the room temperature resistances is from several kΩ to several hundred kΩ as stated earlier. Besides, we have experimentally found that the success rate for different sensor chips is consistent with overall success rate, which is equal or greater than 70%. The success rate is defined as the ratio of the number of successful CNT-connected microelectrodes to the total number of microelectrodes on a substrate. Since the volume of each drop of the CNT/ethanol solution in the experiment is not consistent, the yield of the batch assembly of the bundled CNT cannot be 100% based on our current rudimentary technique. However, the batch AC electrophoretic manipulation of bundled CNT is efficient and reliable based on our experimental validation, and the yield can be further improved by using a more precise injection system, which will be described in the later section.

III. CNT AS SENSING ELEMENTS

With the ability to batch manipulate the bundled CNT to form resistive elements on patterned substrates, we have investigated the possibility to utilize the bundled CNT as sensing elements for thermal sensing. The bundled MWNTs as sensing elements for micro thermal sensors can be driven by a simple constant current circuit. An experiment for investigating the temperature dependence of the bulk MWNT sensor was performed. The fabricated sensor chip was packaged on a PCB for data acquisition and was put inside an oven. Then, the resistance change of the MWNT sensors was measured as the temperature inside oven was varied. The temperature-resistance relationship for the MWNT sensors was measured and a representative data set is shown in Fig. 6 for several cycles of measurements. The temperature-resistance dependency of bundled MWNT implies its thermal sensing capability. Based on experimental results, the range of the temperature coefficient of resistance (TCR) for the MWNT sensors were found to be from -0.04 to -0.07 $\%/^{O}C$.

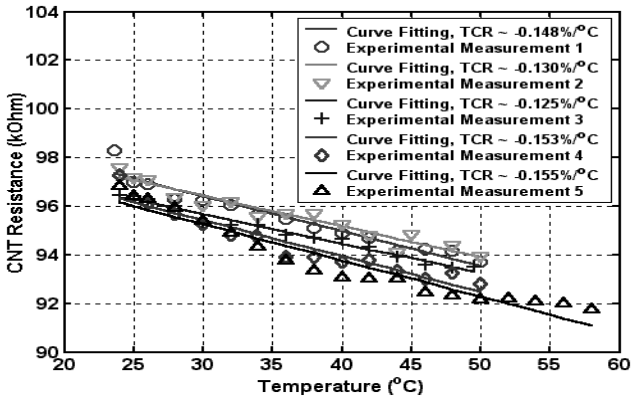


Fig. 6. TCR variations of a typical MWNT device in five consecutive measurements. The experimental data are linearized for the approximation of TCRs.

The I-V Characteristic of the MWNT sensors was also investigated. From the results of experiments conducted on the MWNT sensors, the current required to induce self heating of the MWNT devices was in μA range at several volts, which suggests that the power consumption of these devices is in the μW range (see Fig. 7).

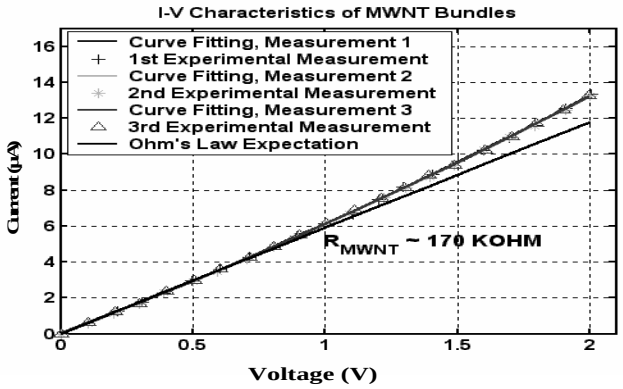


Fig. 7. I-V characteristics of the MWNT bundles. Three repeated measurements were performed to validate the repeatability. The straight line is the theoretical expectation using Ohm's Law and the room temperature resistance of bundled MWNTs in our testing sample was about 170kΩ.

Investigation on the frequency response of the driving circuitry with bundled MWNT as feedback resistor was also carried out. To test the frequency response of the MWNT sensors, input square wave of 3V peak-to-peak various frequencies was fed into the negative input terminal of the circuit and the output response was observed on an oscilloscope. From our experimental measurements, bundled MWNT sensors exhibited very fast frequency response (about 148 kHz). As a comparison, typical frequency response of MEMS polysilicon sensors in constant current mode configuration without frequency compensation is around several hundred Hz to several kHz [10][11].

IV. Automated CNT Microinjection/Spotting System

Based on the results of CNT formation by using AC electrophoresis process and the thermal sensing capability of the bundled CNT sensors, our group envision that if a systematic and rapid fabrication technique can be developed, CNT based commercial sensors may be realizable in the future. We are now developing a computer-controlled CNT microinjection system to perform the dielectrophoretic manipulation of CNTs automatically, i.e., ultimately, the CNT/ethanol solution could be ejected to the microelectrodes precisely, and the volume of CNT/ethanol droplet could also be consistently controlled. Successful development of this system will improve the yield of the batch assembly of the CNT devices significantly.

A. System Architecture

The preliminary prototype of the CNT microinjection system is illustrated in Fig. 8. It mainly consists of three parts: motorized manipulators, a set of video microscope system, and a computer. The whole system is installed on a vibration isolation table. Essentially, a chip with sensor-microelectrodes and the ethanol/CNT solution are placed on a x-y motorized plate. A *nano probe* fabricated using the technique developed by our group in [12] is fixed on another manipulator and moves in z direction, which is used to transfer the solution to the microelectrodes. In order to check the precision and quality of solution spots on the chip substrate, a video microscope is implemented to observe the position of the microelectrodes on the chip. Note that the conceptual system shown in Fig. 8 is for a system based on the "spotting" technology developed for the DNA chip industry. However, it is not clear now either using a "spotter" or a "micro-injector" (using a high-pressure syringe to dispense a solution) is more suitable for CNT solutions. Hence, our group is currently exploring both options.

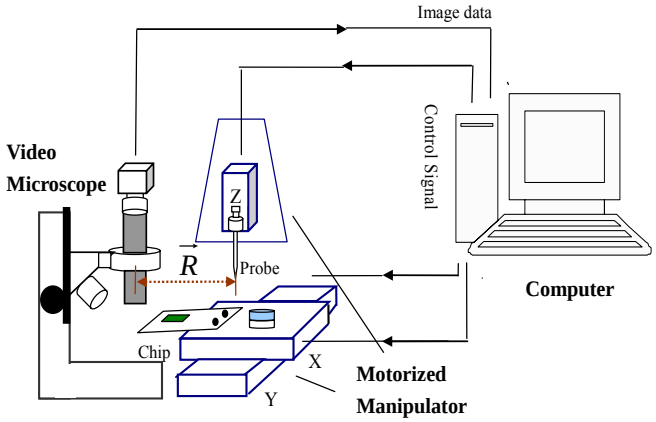


Fig. 8. The architecture of the automated CNT microinjection system.

There are several technical problems that must be addressed to develop our custom-built automated system. A more traditional problem, which has long been addressed by the IC manufacturing industry, is described below. In a later sub-section, a more bio/nano technology related problem that is still not fully solved by the bio or nano engineers will be discussed, i.e., the *adhesion* of a solution droplet to an injection capillary.

Before the injection/spotting process, calibration is needed to obtain an exact relative position between the field of view of the microscope and the accurate X-Y-Z framework, which is denoted by $\vec{R}$ shown in Fig. 8. Note that $\vec{R}$ is three dimensional, i.e., $\vec{R}$ =(*Rx*, *Ry*, *Rr*), representing the distances in X and Y directions, and the rotation angle. A method for obtaining $\vec{R}$ is illustrated in Fig. 9. To implement this, a sample chip for calibration is first put on the X-Y stage, and the position of the chip is set as the origin. Afterwards, the nano-probe attached to the Z-stage is moved downwards to transfer a solution droplet onto the chip. The X-Y stages are then moved and the probe spots/ejects another droplet on the chip. By repeating this process several times, a matrix of droplets is obtained ($\sum_1$ in Fig. 9). The X-Y stages are then commanded to move to the field of view of the microscope, i.e., $\sum_1$ is moved to $\sum_2$, which is observed in the screen

as $\sum_3'$. The angle *Rr* is the angle between the digital video and the microscope. The matrix of the droplets is observed in the screen and noted as $\sum_3$. During the movement of X-Y stage described above, the moving distance is recorded and noted as *Rx* and *Ry* for X and Y directions respectively. Thus, the exact relative position $\vec{R}$ is obtained.

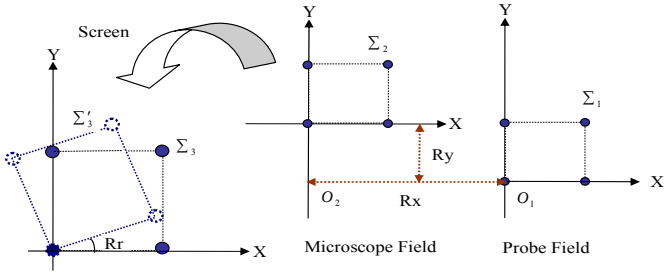


Fig. 9. Illustration of calibration of the CNT microinjection system.

After obtaining the relative position $\vec{R}$ of the sample chip and the probe, the chip with arrays of electrodes can be put on the X-Y stage and its position is adjusted in the field of view of the microscope so that the relative position of the chip and the probe is same as the position $\vec{R}$ obtained in the calibration process. Since parameters such as the position of each microelectrode and the distance between the arrays of microelectrodes are defined during the sensor chip design process, the spotting/injection process can eventually be performed by a computer program automatically. For example, the X-Y stages with the chip can be first moved to the relative position $\vec{R}$ such that one of the microelectrodes of the chip is exactly under the nano-probe, then the probe on the Z-stage is commanded to move downwards to deliver a drop of the solution on the microelectrodes. The X-Y stages are then repeatedly moved according the parameters set in the design process and the probe transfers the solution to the rest of the microelectrodes accordingly.

V. Microinjection Experiment

Preliminary experiments were performed to understand the physical interplay during the microinjection process. As mentioned earlier, the surface adhesion force between the nano-probe tip, the chip substrate material, and the solution to be delivered onto the chip is a very important factor in determining the outcome of a microinjection process. The microinjection experimental setup is shown in Fig. 10. It consists of five major components: capillary probe, syringe pump, programmable micromanipulators, CCD video microscope system and a computer. The whole system is installed on a vibration isolation table. This system was built to mainly study the physical phenomenon during a micro spotting/injection process and is, therefore, is not automated as the system described in the previous section, but is equipped with more precise micro-positioners and better micro-video capturing CCD system. Before the injection experiment, a substrate with arrays of microelectrodes was put on a stage. A capillary probe (TSP010150 with inner diameter of 10 μm and outer diameter of 126 μm, Polymicro Technologies) was mounted on a programmable X-Y-Z micromanipulator (MP285, Shutter Instrument Company), which was used to move the probe to the desired positions on the substrate. A syringe pump was connected to the capillary probe and used to eject fluid droplet to the substrate. This simple system was successfully demonstrated to deliver small fluid droplets (~200μm in diameter) to a silicon substrate surface as shown in Fig. 11.

A. Adhesion Force

It was found that the adhesion force between the outlet of the capillary probe and fluid droplet was very large during the experiment, hence a fluid droplet may not be consistently ejected, e.g., as shown in Fig. 12, a droplet may come out from the outlet of capillary probe but stick on the capillary probe until the droplet becomes very large. Experimentally, we have found that the effect of adhesion force can be eliminated by different methods such as reducing the gap distance between the capillary probe and the substrate, increasing the overlap surface area, or vary the injection pressure. For instance, if the probe tip is moved closer to the substrate as shown in Fig. 13, fluid droplets can be ejected consistently when the gap distance is smaller than 30μm.

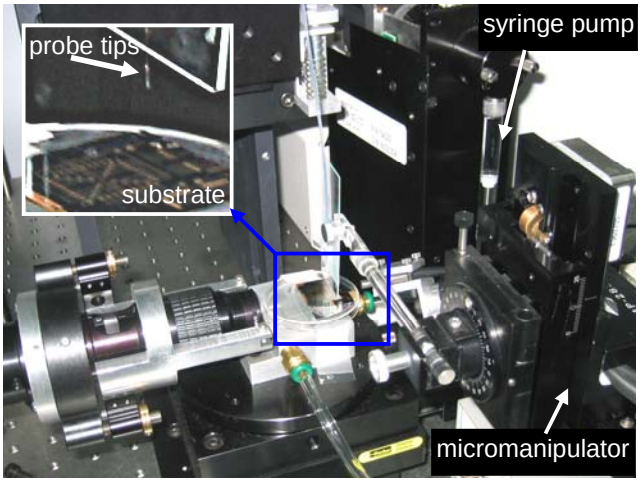


Fig. 10. The microinjection experimental setup.

B. Repeated Microinjection Process

By connecting the capillary probe with a computer controllable syringe pump, the droplet volume can be much more precisely controlled eventually. Currently, we only focused our experiments on the interaction between the solution droplet and the substrate surface, and hence the exact relationship between the droplet volume and applied syringe pressure was not obtained, i.e., in each experiment, a sufficient hydraulic pressure was applied just enough to dispense the fluid to exit the tip of the probe. The microinjection process was tested for its repeatability by moving the probe position using the programmable X-Y-Z micromanipulator to serially deliver several droplets on a test chip. That is, during the experiment, the probe tip was first

moved to eject a droplet to the desired position. Then, it was commanded to move to other positions on the chip surface and repeated the injection process as shown in Fig. 14.

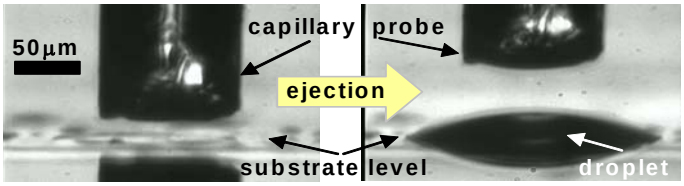


Fig. 11. Microscopic images showing droplet ejection from a capillary probe.

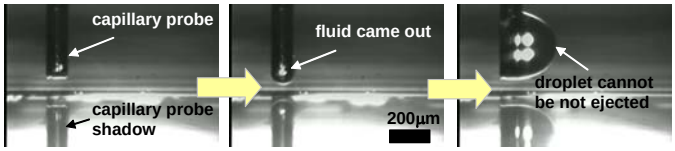


Fig. 12. Microscopic images shown droplet cannot be ejected because of the large adhesion force.

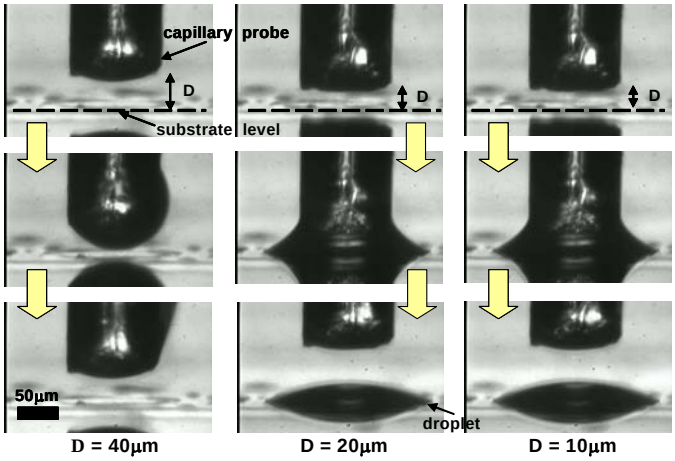


Fig. 13. Microscopic images showing droplets can be ejected by reducing the initial gap distance between the probe tip and substrate. The images in each column represent different trials of initial gap distance. The images in the first row show the initial position of capillary probe. The images in the second row showing the water was ejected from the probe. The images in the third row showing the fluid droplet could be ejected when D = 20 μm and D = 10 μm.

VI. Conclusion

A technique to batch fabricate bundled MWNT device is presented. The TCR measurements of the bundled MWNT based MEMS sensors showed that bundled MWNT can be used as a sensing element with ultra-low-power thermal sensing applications. Also, the architecture of an automated CNT microinjection system is presented. Initial experiments conducted using the microinjection system proved that precise microinjection is feasible to control the volume and position of the solution droplets on a substrate, which will improve the yield and consistency of the batch fabrication of CNT devices in the future.

Acknowledgment

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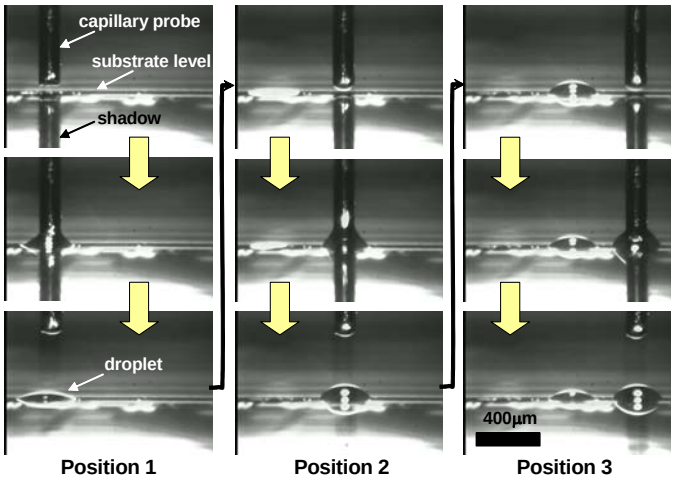

Fig. 14. Microscopic images showing 3 droplets ejected from a capillary probe in a continuous sequence. (The micro droplets are ~200μm in diameter and tend to evaporate very fast due to their small fluid volume.)

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