# Selective local synthesis of nanowires on a microreactor chip[☆]

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## Abstract

This work presents a novel synthesis process for selectively locally growing nanowires on a microreactor chip fabricated by MEMS processes. Nanowires are synthesized in a microchamber by patterned catalysts, reactive gases, and integrated microheaters heating the catalysts to the required temperatures for nanowires growth. Using a field emission scanning electron microscope (FE-SEM) and a transmission electron microscope (TEM), this paper confirms that the synthesized structures are multi-wall carbon nanotubes (CNT). The average diameter of the CNTs is about 16.93 nm and the length is about 100–200 nm. Applying this novel process, the location of the synthesized CNTs can be positioned onto the microheaters in a controllable way. Furthermore, by means of the developed microheater modeling, the chemical vapor deposition CNTs synthesis process can be conducted in low temperature and a low voltage as small as 7 V is required for the microheaters. The proposed synthesis approach makes it possible to integrate CNTs on IC devices by effectively diminishing thermal damage during their growing process.
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*Keywords:* Carbon nanotubes (CNTs); Nanowires; Microreactor; Microheater

## 1. Introduction

The researches on carbon nanotubes (CNT) have received significant attention since it was discovered by Iijima [1]. CNT mainly consist of single- or multiple-walled graphene layers. Using different conditions of chemical reactions or catalysts, it is possible to synthesize single-walled carbon nanotubes (SWNT) or multi-walled carbon nanotubes (MWNT), with radii of about 1–100 nm and lengths of about 0.1–100 μm. The fabrication (synthesis) methods can be classified as three types: (1) the plasma discharging method [2,3], (2) the laser ablation method [4], and (3) the metal-catalyzed thermal chemical vapor deposition method. For the plasma discharging method, DC electric field is applied between two graphite electrodes in a chamber with inert gas, such as hydrogen ($H_2$) or argon (Ar). The CNT is synthesized as plasma discharge occurs between the two electrodes. For the laser ablation method, the focused high-energy beam is used to sublime graphite in a high-temperature furnace in order to form CNT. For the metal-catalyzed thermal CVD method, the CNT is synthesized in a furnace by the pyrolysis of $C_2H_2$ or $CH_4$ with catalysts Fe, Co, and Ni.

The most important conditions to synthesize CNT using the metal-catalyzed thermal CVD method are the process temperature, the catalysts and the reaction gases. At this moment, this synthesis technique is relatively mature. However, the integration of the synthesis process with IC processes is still very difficult [5–8]. It is because the CNT is usually synthesized after IC fabrication processes, and the fabricated circuitry can be easily damaged during the CNT synthesis process which requires high temperature.

Englander et al. [9,10] employed polysilicon microheater device, which is fabricated by MEMS technology, to synthesize CNT on the microheater surface in a traditional CNT CVD chamber. In this work, we develop a microreactor chip by using MEMS processes. This chip consists of metallic microheater structures and a miniaturized CNT CVD furnace, which serves
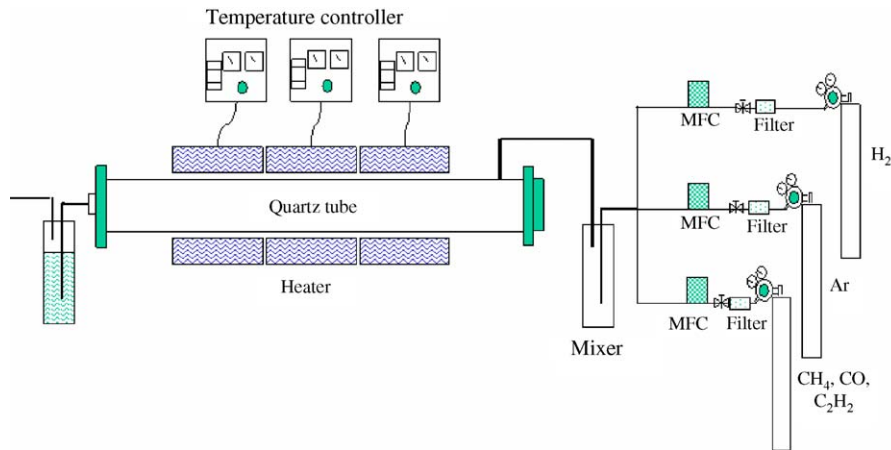
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Fig. 1. A traditional CNT synthesis system.

as a microchamber. CNT can be locally selectively synthesized on the surfaces, which are defined by patterning catalysts using lithography technique. This approach can effectively avoid heating up the whole chip during CNT synthesis so that it is potentially compatible with IC processes [11,12].

## 2. Preliminary experiment results

### 2.1. CNT synthesis conditions

There are many process parameters for synthesizing CNT. Therefore, we use traditional equipment for preliminary study on process parameters [13,14]. Fig. 1 shows the schematic of the synthesis system. The reactor is a quartz furnace of 120 cm in length and 5 cm in diameter, with a heater and a temperature controller (West, 3810). The maximum achievable temperature is 1200 °C, and the maximum temperature elevation rate is 15 °C/min. Without pre-heating, the reactants (Ar, $C_2H_2$, and $H_2$) are supplied to a mixer before entering the furnace. Flow meters (Hastings, Model 400) are used to control the flow rates of the reactants.

A Ni catalyst layer of 30 nm in thickness is deposited and patterned on a substrate. Then the substrate is put into the quartz furnace. As the temperature is stable at 535 °C, Ar gas of flow rate 2000 sccm is supplied into the tube for 10 min. The mixture of Ar and $H_2$ (800/150 sccm) is supplied into the tube for 20 min

before the start of the reaction. Then $C_2H_2$ and $H_2$ (40/150 sccm) is supplied into the furnace for the CNT CVD reaction. After 10 min, the supply of $C_2H_2$ and $H_2$ is stopped, and the heating is also terminated. The wafer can be removed from the furnace for inspection after the system cools down to around 100 °C. Fig. 2 shows the synthesized CNT on the patterned area. The length and the radius of the CNT are about 10 μm and 100 nm, respectively. Based on the preliminary study, the most important process parameters are the minimum reaction temperature, the flow rate of the reactant gases, the mixture-ratio of the reactant gases, and thickness of the catalyst layer.

### 2.2. Thermal analysis for the microheater

We also use the Coventorware to study the microheater's thermal characteristics, such as the temperature–voltage relationship and the optimal dimensions/shapes of the microheater. Fig. 3(a) shows the simulated temperature distribution by the Coventorware. The model includes a Ti layer of 50 μm × 50 μm × 0.5 μm, an Au interconnect layer of 125 μm × 50 μm × 0.5 μm, a nitride layer of 300 μm × 200 μm × 1.5 μm. The thickness of the substrate is 300 μm. The bottom of the substrate is fixed at 300 K. Natural convection effect is also considered in the model. The simulated result is shown in Fig. 3(b). The heater reaches 900 K as the applied voltage is about 2.7 V.
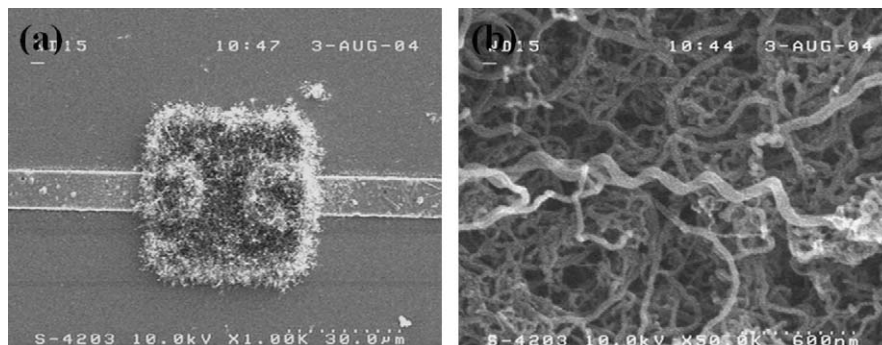


Fig. 2. The CNT synthesized using the traditional CVD method.
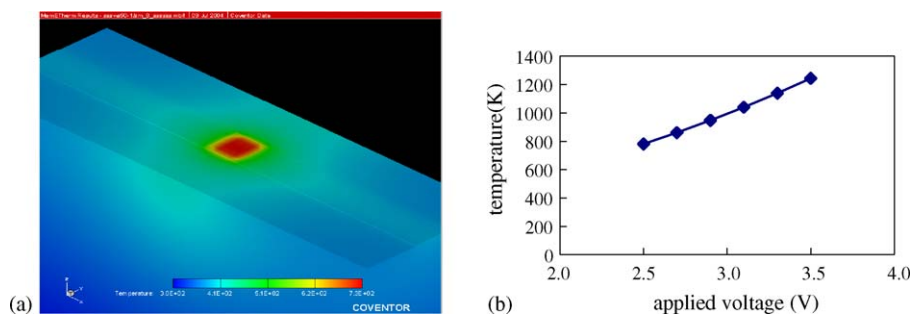
Fig. 3. (a) The solid model and the temperature of the microheater. (b) The simulated temperature-voltage relationship.
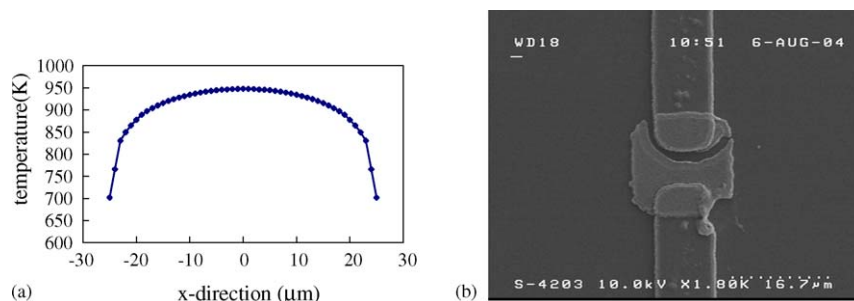


Fig. 4. (a) The temperature distribution on the microheater. (b) The SEM picture of a device that is damaged by an applied voltage beyond the maximum permission.

The spatial variation of temperature on the top surface of a heater (2.7 V) is shown in Fig. 4(a). This figure indicates that the area with relatively uniform temperature distribution is about 30 μm × 30 μm. Fig. 4(b) shows the SEM picture of a device that was damaged by an applied voltage of 5 V. Based on the simulations, the maximum allowable voltage is below 4 V, as indicated Fig. 3(b). Note that the simulated allowable voltage is a little lower than the measured results because the simulations assume that the gases are stationary so that the convection effect is underestimated.

## 3. Microreactor

### 3.1. Fabrication of the microreactor

Fig. 5(a)–(c) show schematics of the components and the integration of the whole device. Fig. 5(a) is the microheater chip, Fig. 5(b) is the cap of the microreactor, and Fig. 5(c) is the packaged device after the heater and the cap is bonded using the anodic bonding process. As shown in the figure, the reactant gases are supplied into the reaction chamber through the inlet. The external voltage source is connected to the microheater through the etched holes on the cap.

Figs. 6 and 7 show the processes of the microreactor chip, which include a surface-micromachining for the microheater, and a bulk-micromachining for a Pyrex-glass cap. For the microheater, two metal layers for the conductive wires, which consist of a 0.5 μm gold film and a 50 nm chromium film, are sputtered and patterned by the lift-off technique. An RIE patterning, which is supposed to prevent the contact problem in the electrodes with microheater, is performed on the nitride layer before the lift-

off process. Then a 0.5 μm titanium layer for the microheater and a 30 nm nickel layer (catalyst) are sputtered and patterned by lift-off. The Pyrex-glass cap is fabricated by the techniques of lithography and laser machining. Finally, the silicon chip is bonded with the Pyrex-glass cap by anodic bonding.

Fig. 8 shows the pictures of the fabricated microreactor device. Fig. 8(a) is the microheater. The smaller picture on the top-left corner is the whole microheater chip. Fig. 8(b) is the Pyrex cap. Fig. 8(c) is the finished product after anodic bonding. The temperature and the voltage for the anodic bonding are 200 °C and 300 V, respectively.
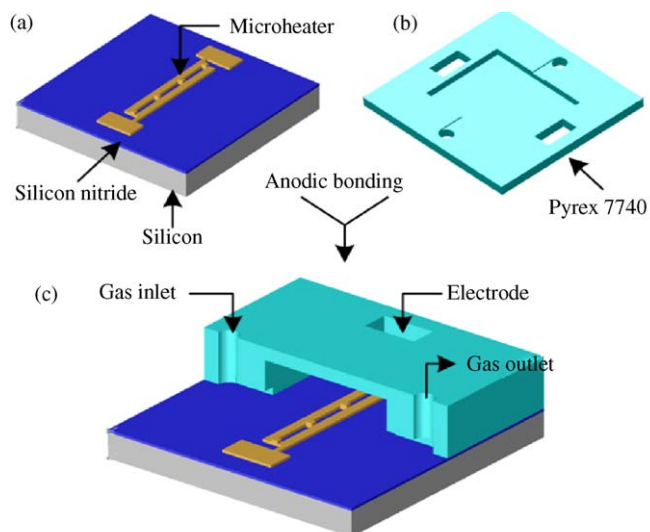


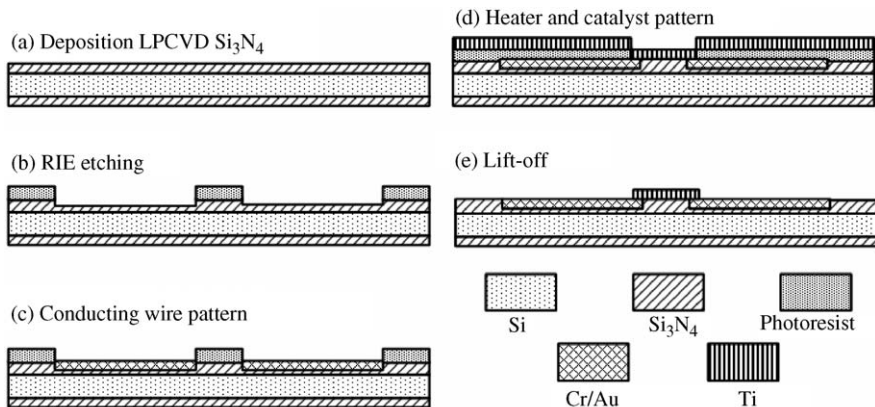Fig. 5. The components and the assembly of the microreactor.

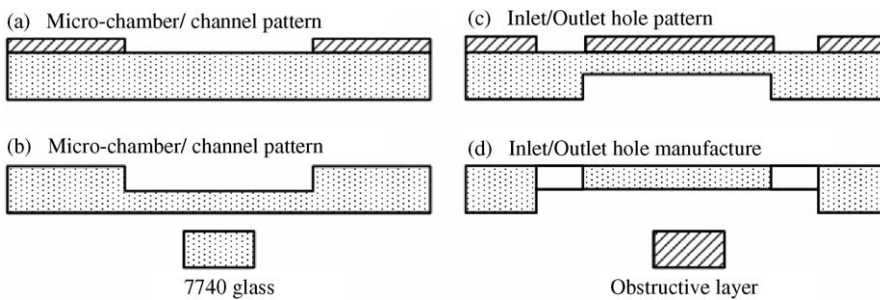Fig. 6.  The process flow of the microheater chip.



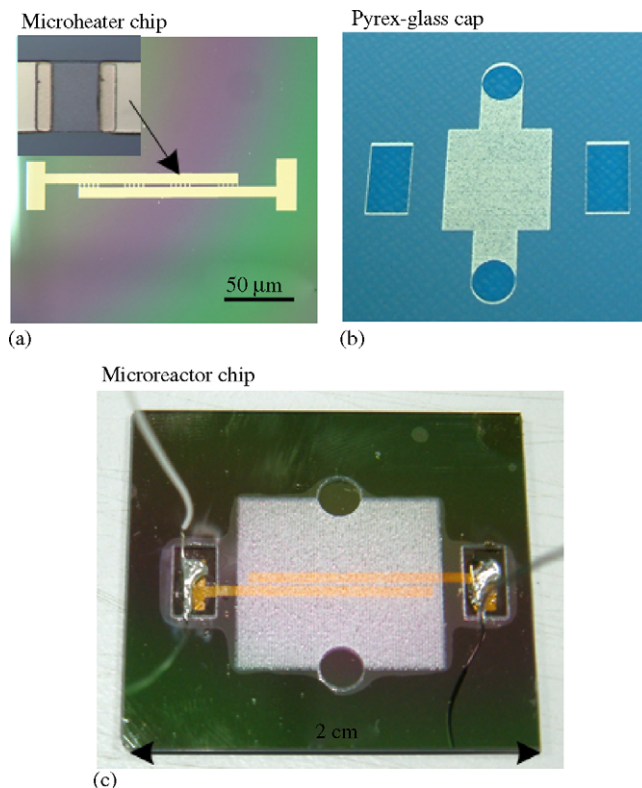Fig. 7.  The process flow of the cap for the microreactor.



Fig. 8.  (a) The microheater. The smaller picture on the top-left corner is the whole microheater chip. (b) The Pyrex cap. (c) The finished product after anodic bonding.
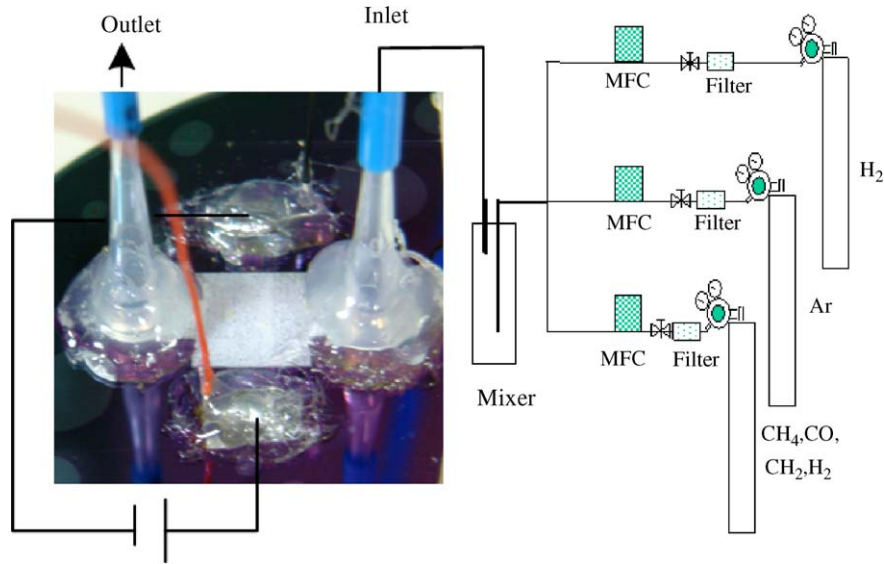
Fig. 9. The experimental setup of the CVD CNT microreactor.

## 3.2. Experimental setup

Fig. 9 shows the experimental setup of the microreactor for the CVD CNT synthesis. Based on the preliminary study of CNT synthesis using a traditional CVD chamber, the reaction process is divided into three steps:

(1) Supplying $H_2$ (10 sccm/min) and Ar (75 sccm/min) for 5 min, and heating the chamber by applying voltage with 0.1 V/s up to 3 V.
(2) Supplying $C_2H_2$ (50 sccm/min), and increasing the voltage from 3 to 7 V with 0.1 V/s for 40 s. The CVD CNT synthesis process starts.
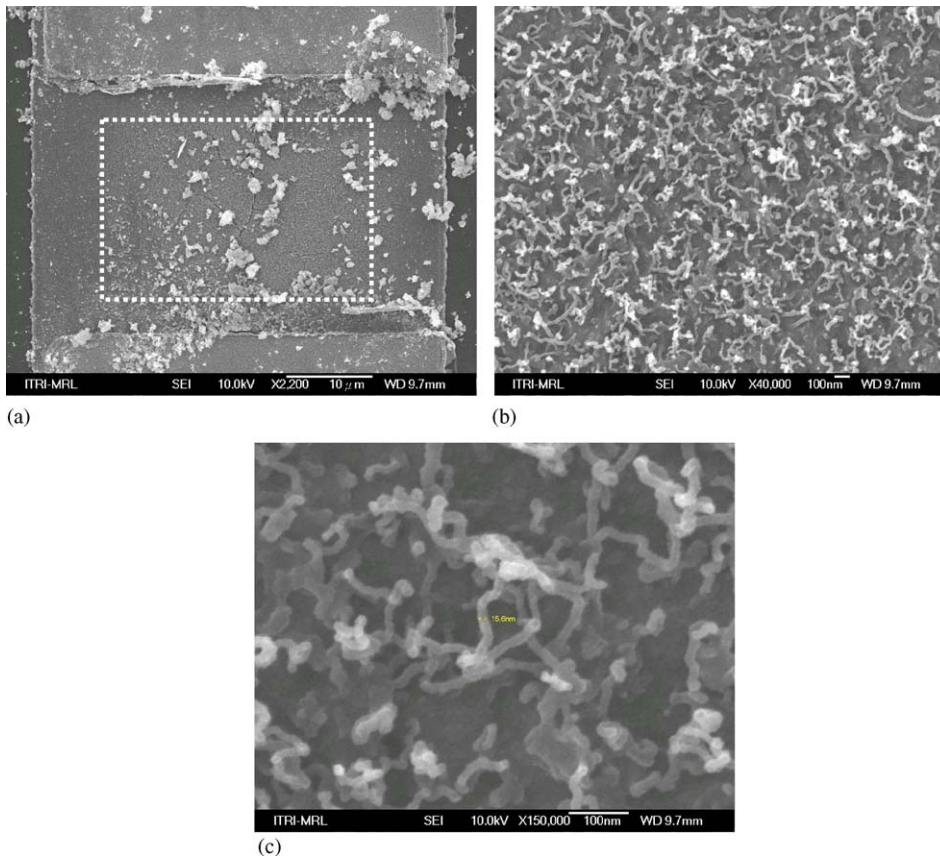


Fig. 10. The FE-SEM pictures of synthesized nanowires using this microreactor.

(3) Stopping supplying $C_2H_2$ and disconnecting the applied voltage. The reactor cools down.

## 4. Results and discussion

The key process parameters are the catalyst, the synthesized gases as well as the heating condition. A voltage of 7 V is applied to the microheater for the reaction of nickel catalyst with the synthesized gases including $H_2$ (10 sccm/min), Ar (75 sccm/min), and $C_2H_2$ (50 sccm/min). Fig. 10(a)–(c) show the synthesized CNT by the microreactor chip. Note that these pictures are obtained using a FE-SEM (JEOL, JSM-6500F). Fig. 10(a) shows the growth of nanotubes is localized on the center region (about 30 μm × 30 μm) of the microheater whose dimension is 50 μm × 50 μm. This result is consistent with the simulated results shown in Fig. 4. Fig. 10(b) is the 40,000-time-magnified picture of the dotted area in Fig. 10(a). Fig. 10(c) indicates that the diameters of the synthesized CNT are about 15.6 nm and their lengths are about 100–200 nm.

Fig. 11 is a statistical dimensional distribution of synthesized CNT from 40 samplings of CNT diameter data. The CNT diam-
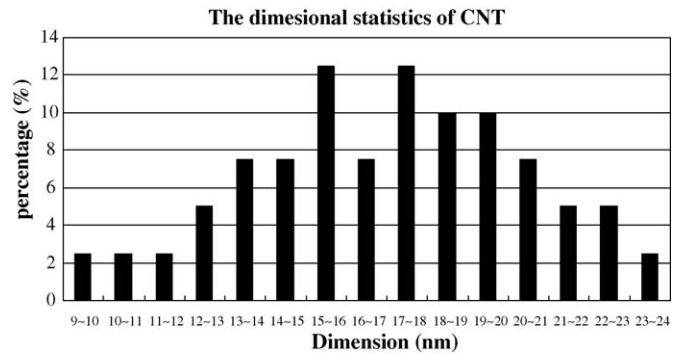


Fig. 11. Statistical distribution of dimension from 40 samplings of the CNT diameter data.

eters distribute between 9 and 24 nm, while higher distributions occur from 13 to 21 nm. Besides, the average diameter of CNT is 16.93 nm and the lengths are about 100–200 nm.

Fig. 12(a)–(c) are the TEM pictures of the synthesized CNT. In order to characterize the CNT crystal structures, a TEM specimen preparation procedure, which includes a T-tool tripod polishing, and low angle (~2°) and low energy (0.5–1 kV)



(a)



(b)



(c)

Fig. 12. The pictures of CNT crystal structures by using a transmission electron microscope (TEM).

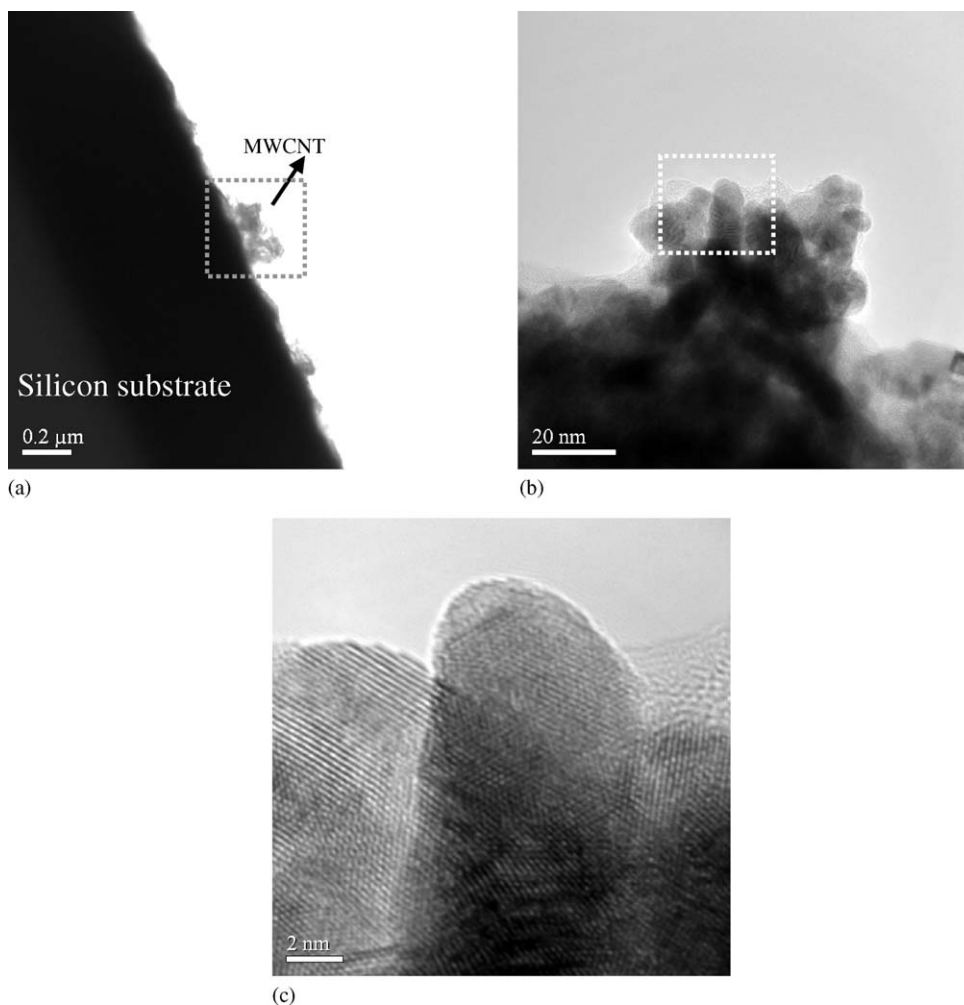ion milling, has been applied. The measurement was performed using a JEOL JEM-2100F transmission electron microscope (TEM), which is operated at 200 kV and is equipped with a Schottky-type field-emission gun. The point-to-point resolution is 1.9 Å. Fig. 12(a) shows the cross-sectional TEM image of the CNT specimen, where the MWCNT are indicated by the arrowhead. Fig. 12(b) is a magnified picture of the dotted area in Fig. 12(a). Fig. 12(c) indicates that the crystal structures are multi-wall carbon nanotubes. The graphite layers of CNT are between 10 and 20 nm. The top ends of these CNT contain the particles of metal carbide or metal catalyst.

Note that the radii and the lengths of synthesized CNT by using the technique in this work are relatively non-uniform when compared with the results by using the traditional CVD CNT furnace. We speculate that this difference is due to the flow behaviors of the reactant gases (e.g., micro fluidic and thermal effects) in the micro reaction chamber. In addition, in our electro-thermal simulation model, we assume that the air surrounding the device is stationary (i.e., natural convection boundary condition). However, in the reaction chamber, the reaction gases flow through the microchannels at certain velocity. Certain portion of the heat generated by the microheater will be dissipated by the "forced convection" effect. Therefore, the gas-flowing effect is the possible reason why the experimental heating voltage is higher than the simulated results. Further study on the gas flow behaviors as well as temperature control is under way.

## 5. Conclusions

This work demonstrates a novel synthesis process for selectively locally growing nanowires on a microreactor chip that is fabricated by MEMS technologies. The developed process allows nano-device engineers to control the location of the CNT materials. The microreactor chip consists of a microheater structure and a micro-reaction chamber by anodically bonding a Pyrex cap on a chip carrying the microheater structure. The microheater contains a titanium layer of 500 nm in thickness and a nickel catalyst about 30 nm in thicknesses. The CNTs were successful synthesized by the low temperature CVD methods on the microheater and only 7 V input voltage is required to be applied on the microheater. The supplied gases, which include $H_2$, Ar, and $C_2H_2$, react with the nickel catalyst to synthesize CNTs. The crystal structures and dimensions of CNT were observed by a FESEM and a TEM. Higher distribution of the synthesized CNT diameters is in the range from 13 to 21 nm. The average diameter of CNT is 16.93 nm. The lengths of the synthesized CNT are about 100–200 nm. Besides, the CNTs grow on the center region (about 30 μm × 30 μm) of the microheater (50 μm × 50 μm), which is consistent with the thermal analysis results.

This work has shown the feasibility of synthesizing CNT in a microchamber by demonstrating the functionality of proposed microreactor chip. This approach is a low temperature process and can effectively avoid heating up the whole chip during the CNT synthesis process. Therefore, it is potentially compatible with IC processes and permits the integration of CNTs to IC devices. The applied voltages to each microheater and the react gases to each microchamber can be controlled separately. This allows the synthesized CNTs can be highly uniform from chamber to chamber and provide the solution to the critical non-uniform problem encountered in large size CNT field emission displays (FED).

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## Biographies

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