

Fullerenes, Nanotubes, and Carbon Nanostructures



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Self-Aligned Growth of Single-Walled Carbon Nanotube Bridging Two Electrodes

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An integrated method for the fabrication of electrical contacts to the single-walled carbon nanotubes (SWNTs) by gas-flowing techniques is reported. Bridge structures containing single SWNT channels are successfully fabricated through the CVD process. Raman spectra of the grown nanowires exhibit typical radial breathing modes which can be associated with the vibrational features of SWNT. Atomic force micrograph (AFM) and scanning electronic microscopy (SEM) images demonstrate that the as-growth SWNTs are indeed bridging two electrodes. I-V curves of such a structure confirm that the SWNTs are electronically linked with the Mo electrodes. This research provides a parallel method for the large-scale integration of SWNTs into electronic, optoelectronic, and sensing systems.

Keywords Single-walled carbon nanotubes, chemical vapor deposition, micro/nano fabrication

Introduction

While significant advances have been made in the controlled growth and separation of single-walled carbon nanotubes (SWNTs), progress in the fabrication of electrical or mechanical contacts to these molecular wires is needed for their large-scale integration into electronic, optoelectronic and sensing systems (1–3). For example, Walters et al. used an atomic force microscope in lateral force mode to study the elastic strains of freely suspended SWNTs and reported a low bond of 45 ± 7 GPa for the tensile strength of SWNT ropes (4). However, the approach they used is not compatible with microfabrication techniques. Using chemical vapor deposition to synthesize SWNTs on catalytically patterned surface, and electron beam lithography (EBL) to define electrically addressable devices based on carbon nanotubes with the length of $2\mu m$, Dai et al. confirmed the possibility to integrate suspended carbon nanotubes arrays into electronic devices (5). The serial nature of the EBL process makes it a costly technique and hence undesirable for the fabrication of arrays of SWNT-metal contacts for future applications. Metal contacts to the SWNTs

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were established using alternating current dielectrophoresis by Takenobu et al. (6), which require the great skill in dispersing nanotubes. Using atomic force microscope (AFM) in noncontact mode, Zhang et al. positioned carbon nanotubes between two gold electrodes at SiO₂ surface to form the IR sensor (7) and reported optelectronics effects in such a carbon nanotube-based device. However, the method is still not suitable for bulk process because it is time consuming and requires manual operation. Controlled growth of Carbon nanotubes (CNTs) with different alignments was achieved using electrically biasing catalyzed electrodes by GYao et al. (8). CNT growth was suggested to be guided by the movement of electrically charged catalyst-nanoparticles under the influence of an external electric field, which needs high voltage and complex equipment. The properties of SWNTs and the methods to prepare SWNT-based devices have been explored (9–11), but an effective strategy to make excellent electrical contact between nanotubes and the micro-electrodes is still a matter of arguments. In particular, it is highly desired to find a simple method to fabricate micro/nanoscale devices based on the carbon nanotubes with controllable position and orientation.

In the present work, we demonstrate that metal contacts can be established on SWNTs by a gas-flowing CVD process. The experimental results demonstrate that the distribution of SWNTs can be controlled by the gas-flowing rates and the sample place.

Experiment

Figure 1 shows the schematic procedures for the growth of aligned SWNT between Mo electrodes. In details, one piece of p-type silicon (100) wafer was thermally oxidized at a temperature of 1100° C to get SiO_2 layer with a thickness of 1 μ m which can be used as an isolation layer. A 50 nm thick Mo film was then deposited on top of SiO_2 layer by sputtering. Subsequently, photolithography and dry-etching techniques (reactive ion

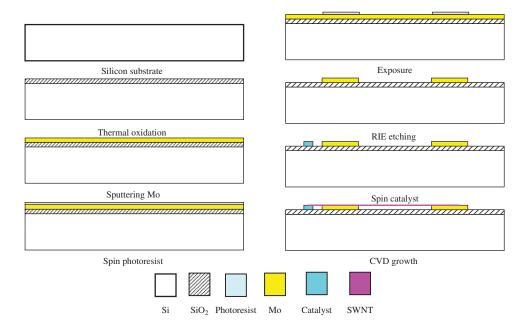


Figure 1. Fabrication process (Figure available in color online.)

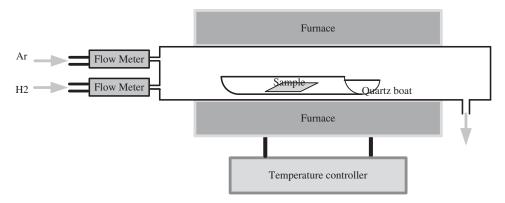


Figure 2. Schematic of the CVD equipment.

etching in SF₆ and CHCl₃ for removing Mo without a photo-resist protection) were used to form opposing Mo electrodes. The sample with electrodes was put into chemical vapor deposition (CVD) furnace via quartz boat.

SWNTs were synthesized on SiO₂/Si substrates with prepatterned electrodes using gas-flow methods in a CVD system. The equipment was illustrated in Figure 2. The CVD process includes catalyst-assisted decomposition of hydrocarbons such as ethylene or acetylene. In a tube reactor at a temperature of 750–1050°C, the growth of carbon nanotubes over the catalyst was finished by cooling the CVD system (12). The quality of CNTs was affected by many factors, including the carbon source for the synthesis of CNT, the preparation of catalyst, the grown atmosphere in the reaction chamber and the flow rate of air (13). In this paper, 0.01M FeCl₃ ethanol solution was applied by micro-contact printing to the area near one electrode, and this can be served as catalyst. The wafer was then placed in a horizontal 1.5-inch quartz furnace with the catalyst end directed towards the gas flow. The temperature was at 900°C, and the flow of Ar/H₂ was 500sccm/30sccm, respectively. Ethanol was introduced into the furnace by bubbling 200sccmm Ar through the ethanol. The gas-flowing velocity could be in-situ controlled and measured by the flow meter. Following the procedure of CVD, CNTs were grown from one electrode to opposing electrode to from a bridge by catalytic CVD of ethanol. The growth direction of the CNTs was decided by the direction of the gas flow. Under these conditions, most of the carbon nanotubes are single-walled, which was described in another paper (14).

Results and Discussion

The structure of the nanotubes obtained from the ethanol-based reactions was characterized by using a field-emission scanning electron microscope (Hitachi S4700 FESEM system, with a resolution of 1.2 nm at 35 kV). An AFM probe station SPI-3800N (Seiko Instruments), a micro-Raman spectrometer with an argon laser, and a high voltage source-measurement unit (Keithley 237, with a 100 pA measurement resolution).

Figure 3 shows typical scanning electron micrographs of the SWNT bridges fabricated by the CVD process with gas-flow controlling techniques. Figure 3(a) shows the aligned line-like structures come from the catalyst area, and the length of the nanotubes was estimated up to 1mm. Figure 3(b) shows a SEM image of opposing electrodes. A SWNT is clearly observed to bridge the electrode pair. The direction of gas flow is from the left electrode to the right electrode. The length of the SWNT was determined by the electrode

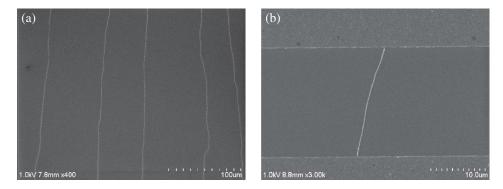


Figure 3. SEM of grown CNTs.

gap distance. By changing the separation between the electrodes, the length of nanotube could be controlled.

Figure 4 shows an AFM image of the samples in air and at room temperature, which characterizes the diameter of the carbon nanotube synthesized by CVD. The diameter of CNT was estimated at \sim 1.5 nm as indicated in Figure 4.

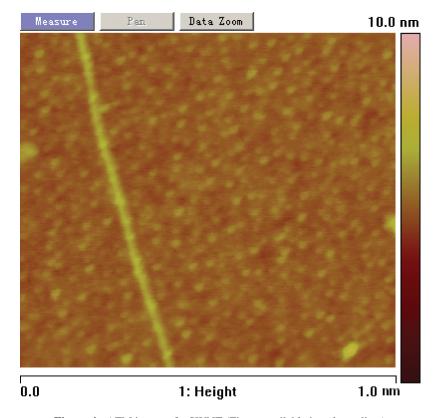


Figure 4. AFM image of a SWNT (Figure available in color online.)

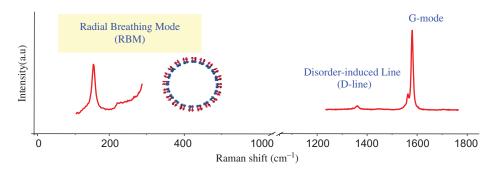


Figure 5. Raman spectra of SWNT (Figure available in color online.)

Figure 5 shows a typical Raman spectrum of an SWNT-bridge. Raman scattering spectra excited by a 514.5 nm laser reveal the typical radial breathing modes. Both a sharp RBM peak and a large G-band to D-band ratio clearly indicate the existence of the SWNT (11). These peaks are in excellent agreement with the radial breathing vibrational modes observed previously, and therefore can be used as a fingerprint to identify the carbon nanotube structure in this study. The RBM peak was observed at 168.06 cm⁻¹. According to the relationship between the SWNT diameter (dt) and the RBM frequency (ω RBM) for isolated SWNTs (11), ω RBM = 248/dt, the SWNT diameter is estimated to be 1.48 nm, which is in accordance with the result of AFM image.

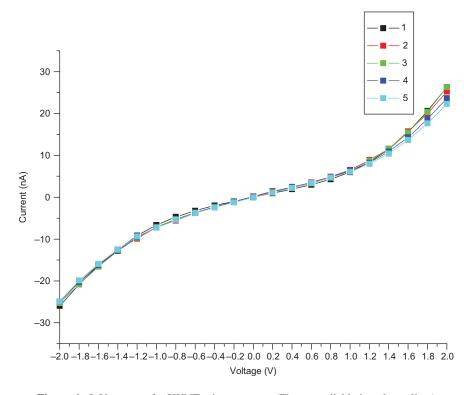


Figure 6. I–V curves of a SWNT microstructure (Figure available in color online.)

Figure 6 shows typical current–voltage (I–V) characteristics of the SWNT-bridge structures. The electrical properties of the samples formed by individual nanotube between Mo electrodes were further characterized at room temperature by measuring electrical resistance. The scan voltage is from -2V to +2V with the step of 0.2V. We measured the sample several times and the results were reproducible. The curves show symmetric characteristics which resemble the nonlinear I–V characteristics of the SWNTs as reported (15). The SWNT-bridge structure can be modeled as a metal–semiconductor–metal (M–S–M) structure which is composed of two Schottky barriers connected back to back, in series with a semiconductor. Five runs of the measurements which were shown in Figure 6 gave almost same I–V curves, indicating that the excellent contact between the nanotubes and Mo electrodes have been formed using our processing method in this paper.

Conclusion

In summary, we developed a method to directly grow long SWNTs bridging two electrodes. The oriented growth of SWNTs can be finished using gas-flow techniques. This opens possibilities to the integration of nano-material with microstructure device, and all the processing techniques are compatible to the standard semiconductor processing. In the future, on-going work includes optimization of the synthesis condition to increase the growing efficiency. In addition, controllable growth of SWNT with the desired characteristics remains to be addressed. Further study will focus on the synthesis of SWNT on the desired area of microstructure to form the practical electrical and nano-electro-mechanical systems based on nanotubes.

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