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Fabrication of Individual Carbon Nanotubes and Their Arrays in a Transmission Electron Microscope

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ABSTRACT

In this study, we present an approach to manufacture individual and array-type carbon nanotubes in a transmission electron microscope. Semiconductor nanowires are used as templates to form a core-shell structure by depositing uniform amorphous carbon layers around the nanowires using electron-beam induced deposition. Joule heating produced by an applied external voltage melts the nanowires and crystallizes the amorphous carbon layer into nanotubes within a commercial in-situ scanning tunnelling microscope-transmission electron microscope probing system. Using this approach, carbon nanotubes with well controlled wall thicknesses, diameters and lengths have been fabricated. In-situ measurements of electrical properties reveal that the resultant carbon nanotubes have a semiconducting resistivity. By the demonstration of producing a nanotube array, this proof-of-concept approach opens a new pathway to fabricate high-performance carbon nanotube arrays with controllable morphology for practical applications.

1. Introduction

As a key building block for solid nanodevices, carbon nanotubes (CNTs) have been studied extensively in recent decades due to their unique physical properties, such as ballistic transport characteristics,[1] high carrier mobility,[2] capability of carrying large current density,[3] and exceptional mechanical properties.[4,5] These advantages make CNTs popular building blocks for nanoscaled devices.[6-14] Although fabrication of CNTs has advanced considerably in the past two decades, it is still a challenge to manipulate CNTs to connect between two electrodes for two reasons. One is their very small size, the other is that the fabricated CNTs are easily tangled when they are fabricated by traditional methods, such as arc discharge,[15,16] laser ablation,[17] and chemical vapour deposition (CVD).[18-20] A recent unconventional study showed that an integrated CNT array containing graphitic electrodes and interconnects were formed directly from their synthesis,[21] but precise control of the quantity of the as-grown CNTs is still challenging. In the past decade, several studies have shown that an alternative strategy is to fabricate CNTs via a phase transformation induced by heating rather than growth.[22-25] Furthermore, in-situ transmission electron microscopy (TEM) investigations show that the phase transformation from amorphous carbon to sp² structured carbon can also be induced by applying a voltage.[26-28] The latter approach has the merit of controlling the
quantity easily and the location precisely. However, this strategy have not attracted much attention because it is very difficult to secure high quality CNTs.[28] Compared with traditional methods, it is difficult to control the length, diameter, thickness of such CNTs because of poor carbon precursors used as the starting material.

In this study, we demonstrate an improved approach to achieve better carbon precursors for fabricating CNTs in which undoped InAs nanowires are used as templates (cores) for depositing amorphous carbon shells as the precursors via electron beam induced deposition. By applying an external voltage between two electrodes of the core-shell nanostructures, the resultant Joule heating can melt the nanowire cores and crystallize the amorphous carbon shells into CNTs. By controlling deposition duration and selection of nanowires with desired morphology, CNTs with different wall thicknesses, diameters and lengths can be fabricated. This approach has also been extended to fabricate a CNT array between two electrodes inside a TEM. This proof-of-concept work could be helpful to design nano-devices based on individual CNT or array.

2. Experimental

2.1 TEM characterization and observation

JEOL-2010 and JEOL-2010F TEMs were used to characterize the structure and observe the in situ structural evolution. The operation voltage is 200kV.

2.2 Manipulation of nano-materials in TEM

A commercial scanning tunneling microscope-transmission electron microscope (STM-TEM) joint instrument (Nanofactory TM) inserted into a TEM was used to carry out the manipulation of nano-materials. Usually, a fresh tungsten tip is fixed on the movable end of a piezo-motor and this tip can achieve movement precisely in three dimensions via adjusting the controlling system. More details can be found in our previous publications [29-33].

2.3 Electron beam induced deposition (EBID) technique
In this work, EBID technique was used to bond the selected nanowires to tungsten tips and to form a uniform carbon layer surrounding the nanowire. EBID is caused by the dissociation of molecules adsorbed to a surface by high energy electrons, and has demonstrated by many literatures [34,35].

2.4 Electrical measurements

Scanning tunnelling microscope-transmission electron microscope (STM-TEM) system can be used to measure the current-voltage (I-V) curves of bonded nanomaterials between two electrodes. The maximum sweeping voltages are ranged from -10V to +10V. This system can also change to another mode, through which, maximum bias voltage up to 140V can be applied.

2.5 Preparation of InAs nanowire array

A dual beam (ion beam and electron beam) system (FEI Helios 600) was employed to fabricate nanowire arrays by cutting a small piece of wafer with epitaxially grown InAs nanowires and welded the wafer on a tungsten electrode.

3. Results and discussion

Figure 1 schematically illustrates the experimental setup and process. Firstly, InAs nanowires were picked-up by a gold wire via the Van der Waals force (see Figure 1a), and the Au wire was fixed in the probing system and inserted into the TEM. A suitable nanowire was then selected, and picked up from the gold wire using a tungsten probe connected with the movable piezomotor adjusted by the STM-TEM controlling system. Contact between the selected nanowire and the tungsten probe was made using the EBID technique, as illustrated in Figure 1b, and the tungsten probe was then moved away from the Au wire (Figure 1c). After that, the Au wire was replaced by a second tungsten tip as another electrode and welded by EBID, as shown in Figure 1d. Figures 1e - 1g show a process to coat amorphous carbon around the nanowire via electron beam irradiation (Figure 1f) and to melt and transfer out the core by applying an external bias voltage owing to the significant built-up of Joule heating as schematically sketched in Figure 1g. Simultaneously, the Joule heating also crystalizes the amorphous carbon precursor shells into CNTs.
Figure 1. Schematic map illustrating process of formation of a single CNT. (a)-(d) showing how to select and fix an individual nanowire (NW) between two W tips using STM-TEM; (e)-(g) showing the process to form a core-shell structure based on the fixed NW using EBID and a CNT by increasing the bias voltage.

Figure 2 shows a series of TEM images taken from a typical example. Figure 2a is a low-magnified TEM image showing two tungsten tips connected by a nanowire. Figure 2b is an enlarged TEM image and shows a nanowire with two ends fixed by two tungsten tips. Figures 2c and 2d are high-magnification TEM images showing details of two end contacts between the nanowires and tungsten tips. As can be clearly seen, the two ends of the nanowire were bonded well with the tungsten tips. Figure 2e and 2f are TEM images taken at different stages of the nanowire under the electron beam illumination. As can be seen from Figure 2e, when the nanowire was initially irradiated under the electron beam, an almost clean surface can be observed. When the nanowire was irradiated under the electron beam for ca. 20 min, a uniform amorphous carbon shell with a thickness of ca. 2 nm surrounding the nanowire was formed (see Figure 2e). Our extensive TEM investigations indicate that the thickness of the amorphous
carbon shells can be well controlled by the diameters of the original nanowires, as well as the strength and duration of the electron beam irradiation.

**Figure 2.** TEM morphology of an individual NW fixed between two W tips using EBID. (a) the whole image of two W tips and NW; (b) enlarged image taken from the yellow region of (a) showing the NW is connected two W tips; (c) and (d) high-magnification TEM images showing the nanowire fixed with W tip by amorphous carbon; (e) and (f) high-magnified TEM images taken from the dashed framed region of (b) at two different times.
When an external bias voltage is applied to such core-shell nanostructures, the InAs nanowire core was melted by Joule heating and expelled from the carbon shell, resulting in unfilled CNTs. Figure 3 shows such a typical process. Figure 3a shows a core-shell nanostructure before applying the bias, while Figure 3b is a high resolution TEM image taken from the red-framed region showing the perfect crystalline core and the amorphous shell. Figure 3c shows the structure after the nanowire core is melted and expelled out the shell driven by electric field [36], resulting in CNT formation (See Supporting Information 1). Figure 3d is a high resolution TEM image taken from the blue frame in Figure 3c, in which well-crystallized multi-walled CNT can be seen.

During this part of the experiment, the external bias is increased slowly with a step of 0.1 V and an interval of 1 minute. In this particular case, no significant structural change of the nanowire occurs for a bias below 2.9 V. When the bias reached 2.9 V, the nanowire core disappeared immediately. It should be noted that, in order to minimize the irradiation effect, the electron beam must be spread, so that a minimum electron beam effect can be maintained during applying for the external bias. The corresponding I-V curves were also measured accordingly. Figure 3e show the measured result, in which the applied voltage was swept from -100 mV to 100 mV. As can be seen, both curves exhibit linear relationships indicating ohmic contacts. Red and blue I-V curves represent the electrical properties of core-shell structure (Figure 3a) and CNT structure (Figure 3d), respectively. This data reveals a huge difference in electrical properties between the core-shell structure and the CNT structure. Accordingly, we can calculate the resistivity ($\rho$) of CNTs using

$$\rho = \frac{RS}{l} ,$$

where $S$ is the cross-sectional area of the CNT, $l$ is the length of CNT, and $R$ is the resistance. In the case shown in Figure 3, the thickness of the CNT shell is 5 nm, the diameter of the nanowire is 32 nm, the length of the CNT is ~500 nm. Using the obtained $R=V/I=1\times10^7 \text{V/A}$ (based on Figure 3e), $\rho \approx 2 \ \Omega\text{•cm}$ can be obtained. This value is far higher than the reported metallic CNT resistivity of $10^{-6} \Omega\text{•cm}$.[37] Therefore, our fabricated CNTs should have the nature of a semiconductor.
Figure 3. CNT formation process using InAs NW as a template and associated electrical measurements. (a) A low magnification TEM image shows the InAs NW and amorphous carbon layer core-shell structure, (b) HREM image taken from the red framed region in Figure 3(a); (c) A multi-walled CNT was formed when the applied voltage reached 2.9 V, (d) HREM image indicating layer structure taken from the blue framed region in Figure 3(c); (e) red and blue I-V curves corresponding to (a) and (b).

To control the thickness of amorphous carbon precursors, we alter the deposition duration while keeping the deposition strength constant. Figure 4 shows the case of a nanowire with a diameter of 42 nm and a length of 1220 nm. After ca. 1 hour electron beam irradiation (using the low beam density setup), a thicker shell of ~20 nm was formed, as shown in Figure 4a. We then
applied bias voltage between two tungsten tips. With increasing bias, the core-shell nanostructure remains unchanged below 17.2 V (Figure 4b). When the bias reaches 17.2 V, however, most parts of nanowire core disappeared, as shown in Figure 4c. Upon increasing the bias voltage to 17.3 V, more of the remaining the nanowire core disappears (Figure 4d). Taking the case studies shown in Figure 3 and Figure 4 into account, the diameter, length and thickness of fabricated CNTs can be seen to be well controlled. Figure S2 provides another case to demonstrate the fabrication of an individual CNT with a wall thickness of ~10nm (Supporting Information 2).

To understand the fundamental reason of such a phase transformation from amorphous carbon layers to CNT, we note that experimental results [22,23, 26,27] and theoretical predictions [24,25] indicated that this phenomenon can be achieved by heating. If the temperature is sufficiently high, ordered sp2-bonded structures from disordered carbon precursors can be achieved without catalysts. For example, a systematic investigation on the variations of percentage of sp, sp² and sp³ structures with different temperature and initial density of amorphous carbon using molecular dynamics indicates that the sp² structure will dominate upon increasing the temperature up to 2500 K and be above 90% when the temperature is up to 3500 K.[25] The experimental results also indicate the graphitization temperature is 2000~3000°C without assistance of catalyst,[28] while a low temperature is needed if catalysts are used to assist the phase transformation.[26]

In this study, the morphology (length and diameter) of the templating nanowires can be intentionally selected for controlling the length and diameter of CNTs. Due to their lower melting point, the semiconductor nanowire cores can be melted first, and further expelled from the carbon shells under the field effect similar to previous reports.[26] Comparing Figure 3 and Figure 4, it can be noted that both nanowire cores have a similar diameter, but the nanowire shown in Figure 4 is almost 2.5 times longer in length than that shown in Figure 3. Therefore, the resistance of the nanowire shown in Figure 4 is larger, so that a higher corresponding applied voltage is needed to provide sufficient heat to melt the nanowire cores. In order to reduce the external applied power, the nanowire cores should have a smaller resistance and lower melting point. In this regard, InAs nanowires, with a low bandgap of 0.36 eV and a melting point of 943°C,[38] are ideal templates for fabricating CNTs. We also studied SiC nanowires (a bandgap
of 2.4-3.3 eV and a melting point of 2830 °C)[39] as templates to fabricate CNTs. With SiC nanowires there was no observed phase transformation from amorphous carbon to CNT when the applied voltage was below ~110 V. When the applied voltage reached ~110 V, both cores and shells burned simultaneously.

![Figure 4](image)

**Figure 4.** Formation of a CNT at different times as the bias is progressively increased. (a) The initial bias of 0V; (b) the bias is 17.1V; (c) the bias is 17.2V; (d) the bias is 17.3V. In this case, the diameter of the core is 42 nm, the length is 1220 nm, and the average thickness of the shell is 20 nm.

To employ this approach to produce CNT arrays, we use a dual beam (ion beam and electron beam) system to fabricate nanowire arrays by cutting a small piece of wafer with epitaxially grown InAs nanowires and welded the wafer on a tungsten electrode. We performed similar
experiments on arrayed InAs nanowires. **Figure 5a** shows a schematic illustration of a nanowire array connected by two electrodes. Between them, an increasing bias voltage was applied. Figure 5b and 5c are two TEM images showing the samples before and after the bias is applied. Figure 5b shows the InAs nanowire array between two electrodes before applying the external voltage, in which solid nanowires can be seen. In contrast, Figure 5c shows the nanowire array after applying a bias of 2 V. As can be seen, many CNTs were produced by this process. Figure 5d is a high resolution TEM image of the CNT marked by red arrow, indicating a high quality CNT lattice.

**Figure 5.** CNT array fabrication in a TEM. (a) Schematic illustration describing the principle forming a CNT array; (b) TEM image showing a NW array between two electrodes before applied a bias; (c) TEM image after applying a bias of 2V; (d) High-resolution TEM image showing a CNT wall.
3. Conclusion

In summary, by using in-situ TEM approach, we have successfully fabricated individual CNTs using low-bandgap semiconductor InAs nanowires as templates. By controlling the irradiation strength and duration of the electron beam irradiation, and choosing appropriate nanowires as templates, the wall thickness, diameter and length of resultant CNTs can be well controlled. The in-situ measurement of electric properties indicates that the resultant CNTs have a high conductivity. Importantly, we have also demonstrated this approach can be used to fabricate CNT arrays, which provides a pathway for developing CNT arrays with desired morphological control.

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REFERENCES


