

## Multisegmented one-dimensional hybrid structures of carbon nanotubes and metal nanowires

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(Received 22 September 2006; accepted 8 November 2006; published online 15 December 2006)

Multisegmented one-dimensional hybrid structures of carbon nanotubes and metal nanowires were fabricated using the alumina templates. Metal nanowires are first grown inside part of the nanochannel using electrodeposition technique, which is followed by the growth of carbon nanotubes using chemical vapor deposition. Well-adhered interfaces formed between the carbon nanotubes and the metal nanowires. The hybrid structure reported here results in nanoscale metal contact with carbon nanotube and will provide a solution to problem of using carbon nanotubes in interconnects. Nanotube-nanowire interfaces for different metals have also been examined and are characterized using scanning electron microscopy and transmission electron microscopy. © 2006 American Institute of Physics. [DOI: 10.1063/1.2405390]

Template method pioneered by Martin<sup>1</sup> has been shown to be an extremely powerful tool for fabricating one-dimensional (1D) nanomaterials ranging from metal, polymer, and semiconductor nanowires to carbon nanotubes (CNTs).<sup>2</sup> Various advantages have been realized by the template approach. These advantages include the synthesis of the nanowires in large quantity and more importantly, the ability to control precisely the dimension of the synthesized structures and the orientation of the nanostructure assembly.<sup>3</sup> The use of template truly allows one to talk about the spatial arrangement for the nanostructures as it provides a powerful tool to fabricate complex structures that might be otherwise difficult to fabricate using other conventional methods. For example, the synthesis of multisegmented nanowires has been made possible using the templates.<sup>3</sup> Multisegmented nanowires are nanowires which consist of different materials at each segment. While the multisegmented structure can be of different metals,<sup>4</sup> Park *et al.*<sup>5</sup> have demonstrated that multisegmented nanowires of metal and polymer can also be made possible using this method. Applications ranging from electronics<sup>3,6</sup> to biological separation<sup>3,7</sup> have been demonstrated using the multisegmented structures. It is also worth mentioning that although a lot has been done in the synthesis of multisegmented nanowires, relatively little has been done to make multisegmented structures based on nanotubes,<sup>8,9</sup> especially CNTs. However, in comparison to the metal nanowires or polymer nanowires, CNT has superior mechanical and electrical properties. Hence, fabricating CNT hybrid structures by incorporating CNTs in multisegmented structures<sup>5</sup> would certainly result in enhanced properties for

various applications. For example, CNTs are promising candidates for nanoscale electrical interconnects, and they have been shown to carry higher current density than copper nanowires.<sup>10</sup> However, how to effectively contact the metal pins to the CNTs remained as a key challenge. Attempts have been made to directly grow CNT on top of the metal substrate;<sup>11</sup> however, this contact method is only possible for CNT arrays in the bulk form and the method is certainly not applicable to make metal contact to single CNT. As a result, the ability to make true nanoscale interconnects using CNT cannot be achieved using such methods. In this letter, we report the fabrication of two segmented (metal-CNT) and three segmented (CNT-metal-CNT) nanotube hybrid structures of carbon nanotube and metal nanowires using the template approach. Combination of electrochemical deposition and chemical vapor deposition techniques was used to make the hybrid structure. The interface between CNTs and Au or Cu nanowires was examined and compared. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to characterize the hybrid structures. The metal-CNT hybrid structures provide a good metal contact for each single CNT. We believe that our 1D hybrid structure of metal nanowires and CNT will help to pave the way to solve the existing problem of making nanoscale metal contact to CNT for its applications in electrical interconnects.

Self-fabricated alumina templates with pore diameters of about 60 nm were used for all the work described herein. The porous anodic alumina oxide (AAO) templates were prepared by a modified two-step anodizing process reported in detail elsewhere.<sup>12,13</sup> Aluminum (Al) foils were first cleaned by sonication inside the acetone bath. After cleaning, the Al foils were anodized in 0.3M oxalic acid solution at 10 °C under 40 V dc for 6 h. The formed anodic aluminum

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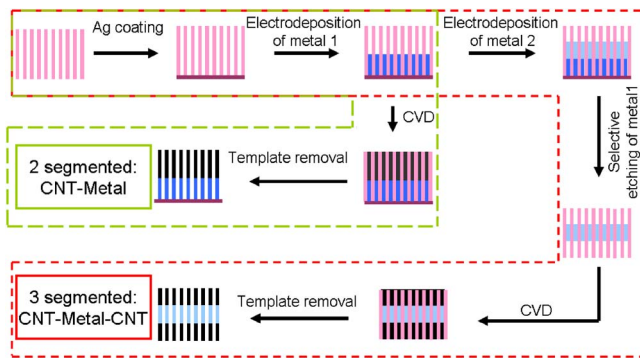


FIG. 1. (Color online) Schematics representing the experimental procedure for the fabrication of two segmented (green line) and the three segmented (red line) metal-CNT hybrid structures.

oxide layer was next removed by immersing the Al foils in a mixed solution of phosphoric acid (6 wt %) and chromic acid (1.8 wt %) at 60 °C for 6 h. After removing the first anodic layer, the second anodization step was carried out under identical conditions to the first anodization. Well-ordered alumina structures were obtained after the second anodization. A saturated tin chloride ( $\text{SnCl}_4$ ) solution was used to remove the remaining Al substrate at room temperature. Finally, the AAO was immersed in a 5 wt % aqueous phosphoric acid solution at 30 °C for 1 h to remove the barrier layer on the bottom side. Templates with nanopore diameters and length of about 60 nm and 35  $\mu\text{m}$ , respectively, were obtained after these steps.

The experimental procedures for growing two segmented (metal-CNT) and three segmented (CNT-metal-CNT) hybrid structures are shown in Fig. 1. First, a layer of Ag coating (about 200 nm) was thermal evaporated onto one side of the AAO template to serve as the working electrode for the consequent electrochemical deposition. The electrodeposition was carried out to deposit metal (Au or Cu) into the nanopores, using the standard three electrode potentiostat system (Princeton EG & G 273 A). Ag/AgCl reference electrode and platinum wire counter electrode were used for the process. The length of the metal nanowire can be controlled by varying the deposition time. After the electrodeposition of the metal nanowires, chemical vapor deposition (CVD) was carried out to grow multiwalled carbon nanotubes inside the template by the pyrolysis of acetylene at 650 °C for 1–2 h with a flow of gas mixture containing Ar (85%) and  $\text{C}_2\text{H}_2$  (15%) at a rate of 35 ml/min.<sup>13</sup> Since the metal nanowires had already filled the bottom portion of the channel, the CNTs would only grow in the remaining top portion which had not been occupied during the electrodeposition step. Hybrid structures with metal nanowire-CNT junctions were formed after the CVD. The sample was plasma etched for about 2 h to remove the amorphous carbon layer on the template surface. Three segmented structure (Au-CNT-Au) has been obtained using a similar procedure. First, Cu was electrodeposited in the nanopores which would act as a sacrificial segment that is to be removed later. Au was then electrodeposited on top of the Cu segment. After the deposition of Au, the sample was immersed in  $\text{HNO}_3$  to selectively dissolve the Cu segment and the Ag back coating. With the removal of the Cu segment, the Au segment would be at the center of the nanochannel with the two ends empty. CNTs were grown on the two empty sides of the Au segment

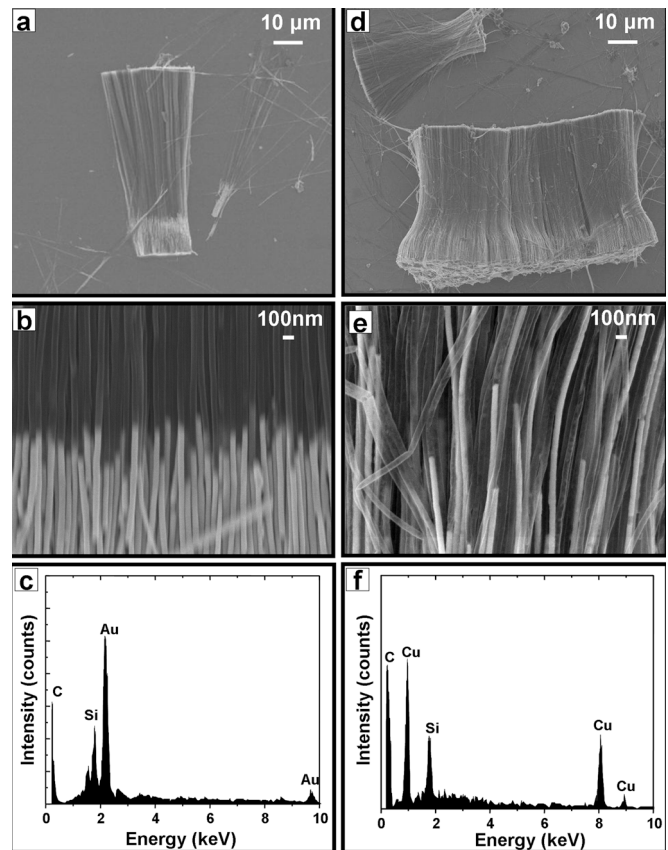


FIG. 2. FESEM images showing the arrays of [(a) and (b)] CNT-Au hybrid structures and [(d) and (e)] CNT-Cu hybrid structures. EDX analysis for the (c) Au-CNT and (d) Cu-CNT hybrid structures dispersed on silicon wafer.

using CVD. After the CVD, three segmented hybrid structures of CNT-Au-CNT were obtained. Plasma etching was carried out to remove the surface carbon coating. Finally, the CNT-metal hybrid structures were released from the AAO template by dissolving the template in 3M NaOH solution for 1 h. The sample was cleaned by rinsing and centrifuging in distilled water for several times. The hybrid structures were then dispersed in isopropanol, and were drop casted on silicon wafer and TEM grids, respectively, for SEM and TEM characterizations.

SEM images of CNT-metal nanowire hybrid arrays are shown in Figs. 2(a) and 2(b) for Au and Figs. 2(d) and 2(e) for Cu. Energy dispersive x-ray (EDX) analysis for the Au and Cu nanowires dispersed on silicon wafer is given in Figs. 2(c) and 2(f), respectively. Unlike the uniform interface between Au and polypyrrole nanowires reported by Park *et al.*,<sup>5</sup> the interface levels between the CNTs and the metal nanowires are not uniform and were shown to vary from one wire to another [Figs. 2(b) and 2(e)]. Before CVD, the metal nanowires were observed to be of uniform height, and the variation in the interface level was observed only after the CVD. Steinhart *et al.*<sup>14</sup> had reported that when polymer melt are in contact with AAO, the adhesive forces (capillary force) provided by the template wall can act to form polymer nanowires or nanotube inside the channel. We believe that same mechanism could be used to understand the height variation of the interface of metal nanowires and CNTs for neighboring channels. During high temperature (650 °C) CVD process, the metal nanowires having lower melting temperature than the bulk metal partially melts and the melted portion of the metal would therefore flow up the

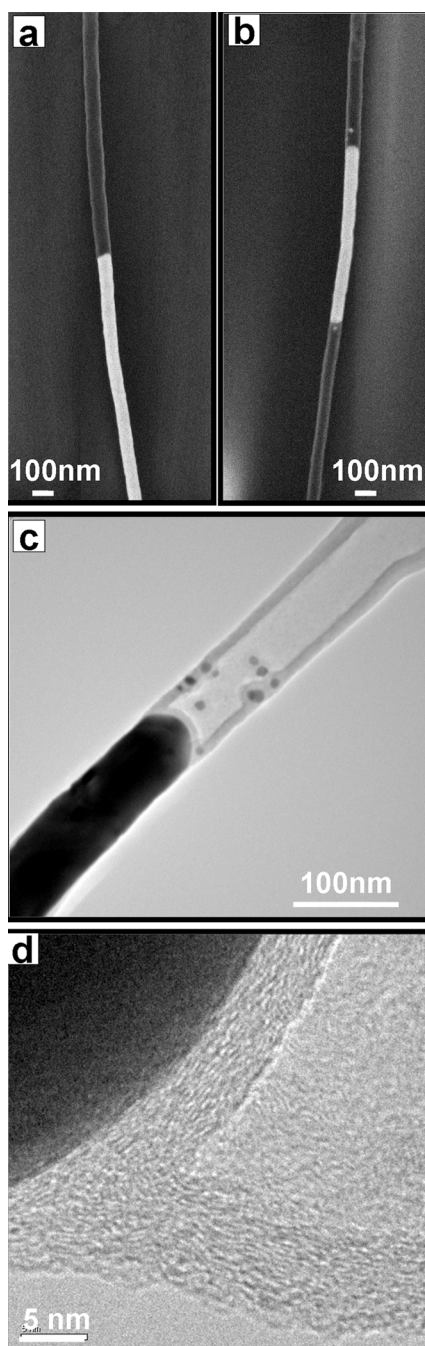


FIG. 3. FESEM images showing single (a) Au-CNT hybrid and (b) CNT-Au-CNT hybrid. (c) TEM and (d) HRTEM images showing Au-CNT junction.

nanochannel with the aid of the adhesive force provided by the template wall and resulted in the difference in interface between each hybrid structure. The interface level for Au nanowires is more uniform [Figs. 2(a) and 2(b)] in comparison to the Cu nanowires [Figs. 2(c) and 2(d)]. The interface level for Au-CNT hybrid structures varies in the range of  $\pm 200$  nm from an arbitrary zero level, while that for Cu-CNT hybrid structures, the interface location varies in the range of  $\pm 1.2$   $\mu\text{m}$ . This variation is due to the difference in melting temperature of the two metals. Since Cu has lower melting temperature compared to Au, larger portion of the Cu nanowires would have melted during the CVD. As a result, greater portion of Cu would have climbed up the template channel resulting in the observed nonuniform interface level.

On the other hand, the melting temperature of Au is much higher. Therefore, less Au (in comparison to Cu) would melt at that temperature, resulting in a more uniform interface level between Au nanowires and CNT.

Field-emission scanning electron microscopy (FESEM) images of a single “hybrid structure” of Au-CNT and CNT-Au-CNT are shown in Figs. 3(a) and 3(b), respectively. From the two images, it can be seen that the interface between Au nanowire and CNT is well adhered. The high resolution TEM (HRTEM) image of the interface between Au nanowire and CNT [Fig. 3(c)] shows the presence of some nanoparticles on the tube wall of the CNT near the junction. This further supports our hypothesis that metal segments at the metal-CNT interfaces had partially melted and therefore was not stable during the CVD process. Also, we can see that the CNT is close ended at the metal junction [Fig. 3(c)]. As reported by Miao *et al.*,<sup>15</sup> closed ended CNT will result if the template is close ended due to the self-catalytic action of the template. Even though the template used in this work is free of barriers, but the metal segment serves as a close ended barrier (cap) to the CVD growth. As a result of the close ended CNTs, a good adherence interface between the metal nanowires and the CNTs is achieved [Fig. 3(d)].

In conclusion, we have fabricated 1D hybrid structures between metal nanowires and CNTs by combination of electrochemical deposition and CVD techniques. A precise control over the length of each segment is possible using this technique. Two different metal (Au or Cu) nanowires were used and the interface level difference between CNTs and metal nanowires was examined in detail. With the well-adhered junction formed between metal and CNT, these structures are likely to help providing a possible solution for making metal contacts to CNTs. More importantly, the metal contacted CNTs remain to be in nanoscale, which is critical for application of CNTs in nanoscale interconnects.

The authors acknowledge the financial support received from the Focus Center New York for Electronic Interconnects and the National Science Foundation Nanoscale Science and Engineering Center for the directed assembly of nanostructures.

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