Zigzag Assembly of Carbon Nanotubes inside Au Microtrenches

Anyuan Cao* and Pulickel M. Ajayan

Materials Science & Engineering Department, Rensselaer Polytechnic Institute, Troy, New York 12180

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We report the self-assembly of zigzag patterns consisting of aligned carbon nanotubes inside Au microtrenches by chemical vapor deposition using ferrocene/xylene solution as the precursor. The zigzag nanotubes have uniform size and constant interpattern distance, which can be controlled by simply changing the width of the Au trenches. We demonstrated the tunable length and orientation of nanotubes during self-assembly, leading to a predictable motion of zigzag patterns. A growth model was proposed for the zigzag assembly of nanotubes, including the formation and subsequent splitting of an amorphous carbon layer on the pattern top. Rows of nanotube micropatterns regularly distributed along the Au trench are potential candidates as integrated arrays of thermal or mechanical detectors and actuators.

Introduction

Patterned carbon nanotube (CNT) architectures enable direct building of hierarchical systems integrating nanotube-based mechanical, electronic, and photonic devices. There has been a great deal of interest in creating predefined CNT patterns with controlled nanotube length and orientation. Typical methods for patterning CNTs in a large area include (1) predeposition of a catalyst film (usually containing Fe, Ni, or Co) by microcontact printing,[1] ink-jet printing,[2] or photolithography[3] followed by nanotube growth from the catalyst, (2) selective growth of nanotubes on a SiO_2/Si substrate (nanotubes grow exclusively on the SiO_2 area),[4,5] and (3) sputtering of a thin metal film such as Au[6,7] or Ag[8] as a mask to prevent nanotube growth in undesired areas. Most of the above methods used photolithography to create patterns on the substrate or mask, and the nanotube growth inherits the pattern profile. However, for these methods, the only way to control the morphology of CNT groups is to preadjust pattern features, and it is difficult to fabricate very small or irregular CNT patterns, or direct CNTs along other directions other than perpendicular to the substrate.

Self-assembly is yet an alternative route for creating ordered nanostructures without prepatterning the substrate. Nonetheless, utilizing this approach to assemble two- or three-dimensional architectures composed of CNTs has been seldom addressed.[9,10] In this paper, we report the formation of zigzag CNT patterns via self-assembly caused by a limited substrate area. We masked a thin metal film by sputtering Au on a SiO_2 substrate and scratched it into narrow trenches and then grew CNTs in the Au trenches by chemical vapor deposition (CVD). We found that CNTs aggregated into regular groups uniformly distributed along the entire Au trench, and the pattern size and distance can be controlled by simply varying the trench width. Furthermore, the orientation of CNTs in each pattern changes while they grow longer, providing a possible way for in situ adjusting the nanotube growth direction.

* To whom correspondence should be addressed. E-mail: caoa2@rpi.edu. Fax: (518) 276-8554.

Experimental Section

Our process for self-assembly of zigzag CNTs involves first making narrow Au trenches on a SiO_2 substrate and then growing nanotubes on these trenches by CVD, as illustrated in Figure 1a. A 20 nm thick Au film was sputtered onto a SiO_2 wafer,[6] and then scratched by a cotton brush containing very fine cotton fibers dipped with acetone. This scratching step created many parallel microtrenches among the Au film where the underlying SiO_2 surface is exposed, and the trench widths range from tens down to less than 1 μm. Here, the exposed SiO_2 surface acts as the growth place for nanotubes and the Au film serves as the mask to inhibit nanotube growth.[6,7] The scratched Au/SiO_2 substrates were then transferred to a horizontal CVD furnace to grow nanotubes. We used the same feeding precursor (ferrocene/xylene) for CVD as reported previously,[4−7] but at a higher reaction temperature of 850 °C. Briefly, 40 mL of ferrocene/xylene solution (0.01 g/mL) was put into a source bottle connected to the inlet of the CVD furnace, and preheated to 150−180 °C to keep the solution boiling inside the bottle. After the furnace was heated to 850 °C under a 200 mTorr vacuum, we opened the source bottle valve to allow the vaporized solution to enter the furnace and grow nanotubes on the Au trenches. The typical reaction time was 3−10 min.

Results and Discussion

Figure 1b shows the scanning electron microscopy (SEM) image of self-assembled CNT patterns inside three parallel Au trenches. Along each trench there are two rows of near-triangular patterns with a zigzag edge exactly fitted to each other. There are three key features in this image: (1) All the patterns in one trench with a uniform width are nearly identical in shape and size. (2) Each row of zigzag patterns extending along the trench has a constant pitch (interpattern distance, marked as P_{zigzag} in Figure 1a). (3) Zigzag patterns grown in the trenches with the same width (the left two) have a similar P_{zigzag}, and those grown in narrower trenches (the right one) show a smaller P_{zigzag}, indicating a strong dependence of the pattern size on the width of the Au trenches (d_{trench}).

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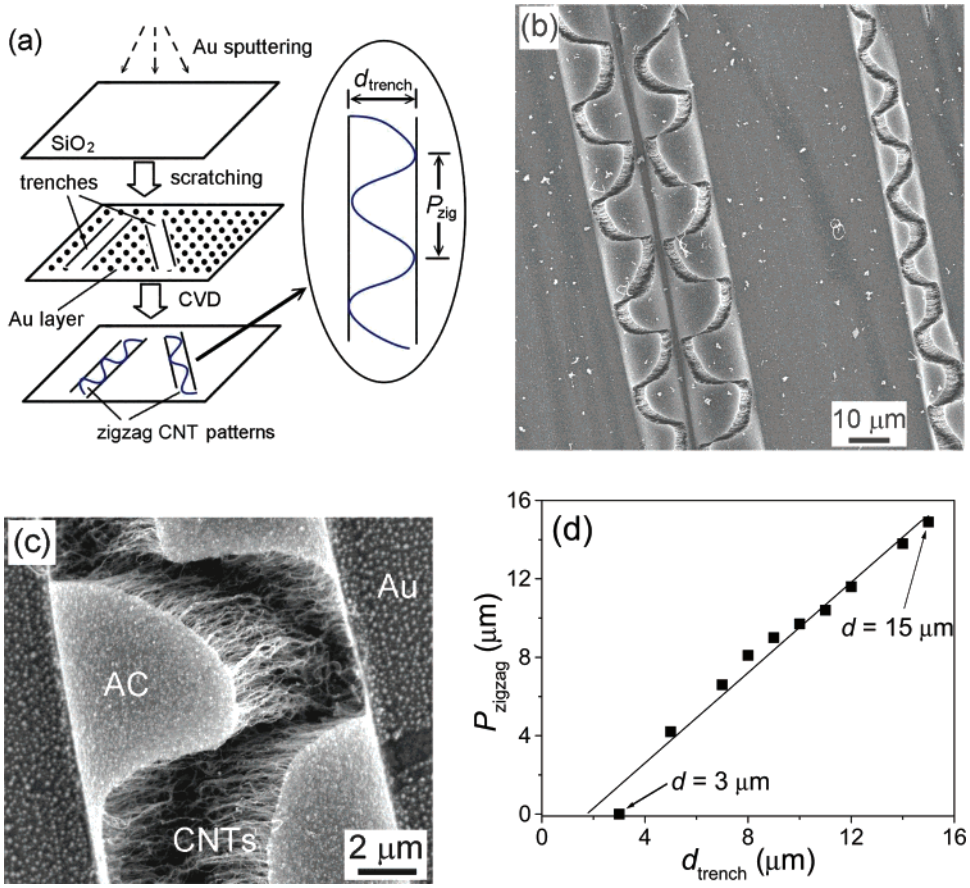

Figure 1. (a) Illustration of the process for making Au microtrenches and subsequent CVD for growing CNTs. (b) SEM image of zigzag CNT patterns self-assembled inside Au trenches. (c) Close view of the zigzag patterns reveals aligned nanotubes, covered by an AC layer. Around the trench are Au particles (white contrast), which serve as a mask. (d) Zigzag pitch (P_{zigzag}) versus the trench width (d_{trench}), showing that P_{zigzag} roughly equals d_{trench} within a trench width of ~5−15 μm.

A close view of the zigzag patterns reveals that they consist of aligned CNTs covered by an amorphous layer (Figure 1c), which split into two half-parts with a zigzag edge, and each "Z" unit holds a bundle of nanotubes at the bottom. The Raman spectrum of the cover layer shows a weak graphite band at 1589 cm^{-1}, and a high disorder band at 1355 cm^{-1}, indicating that this layer is mainly made of amorphous carbon (AC) coming from the thermal decomposition of xylene.

We calculated P_{zigzag} by counting the number of Z units over a 100 μm length for trenches with various d_{trench} values ranging from ~5 to 15 μm, as plotted in Figure 1d. This plot clearly shows that P_{zigzag} increases linearly with, actually very approximate to, d_{trench}. For example, the zigzag patterns grown in a 14 and 7 μm wide trench have an average pitch of 13.8 and 6.6 μm, respectively, suggesting a high correlation between the zigzag pitch and trench size.

When the trench size goes down to ~3 μm, no zigzag trace can be seen (see the arrow in Figure 2a), although there are still aligned nanotubes grown inside (Figure 2b). On the other hand, for the trench width exceeding 15 μm, we observe vertically aligned nanotubes covered by a complete AC layer, again without zigzag pattern formation (Figure 2c). These results indicate that the self-assembly of zigzag nanotube patterns strongly depends on the size of the Au trenches, and happens only in a certain range of trench width (here ~5−15 μm).

We believe that the split of the AC layer on top of the nanotubes results in the formation of zigzag patterns. To confirm this, we carried out CVD at a decreased temperature of 750 °C on the same Au trench substrates. There is no AC layer formed on top of the CNTs, because of reduced thermal decomposition of xylene at lowered CVD temperature (Figure 2d). In this case, we no longer find zigzag splitting of CNTs grown in Au trenches even with the same size range of 5−15 μm. Therefore, the formation of an AC layer is necessary for CNT self-assembly shown in Figure 1b.

On the basis of the CVD and SEM results mentioned above, we proposed a model for self-assembly of zigzag CNT patterns in Au microtrenches, as illustrated in Figure 2e. When the ferrocene/xylene solution vaporized into the CVD furnace at 850 °C, an AC layer first formed due to the xylene decomposition, and covered the Au trenches. Then, CNTs grew from the SiO_2 surface under the AC layer and pushed this layer upward. Indeed, it has been reported that aligned nanotubes can grow under a thin foreign layer deposited on SiO_2 and lift the layer up by continual nanotube growth.[11] The whole AC layer broke into two half-parts as the underlying nanotubes grew longer. For larger Au trenches (>15 μm) which have a relatively large number of nanotubes growing inside, the collective pushing force due to nanotube growth is strong enough to lift the whole AC layer upward, as shown in Figure 2c. For small trenches (<3 μm), the AC deposition is too low to render the subsequent split (Figure 2b). Therefore, both larger and smaller trenches are not suitable for the splitting of the AC layer into zigzag pieces.

To further investigate the growth process of CNTs themselves, we scratched nanotubes from the Au trenches and checked them by transmission electron microscopy (TEM). Figure 3a shows the TEM image of CNTs grown by our CVD process. Most of the CNTs have a diameter of 30−60 nm, and a length up to >10 μm. Detailed examination reveals that the majority of the

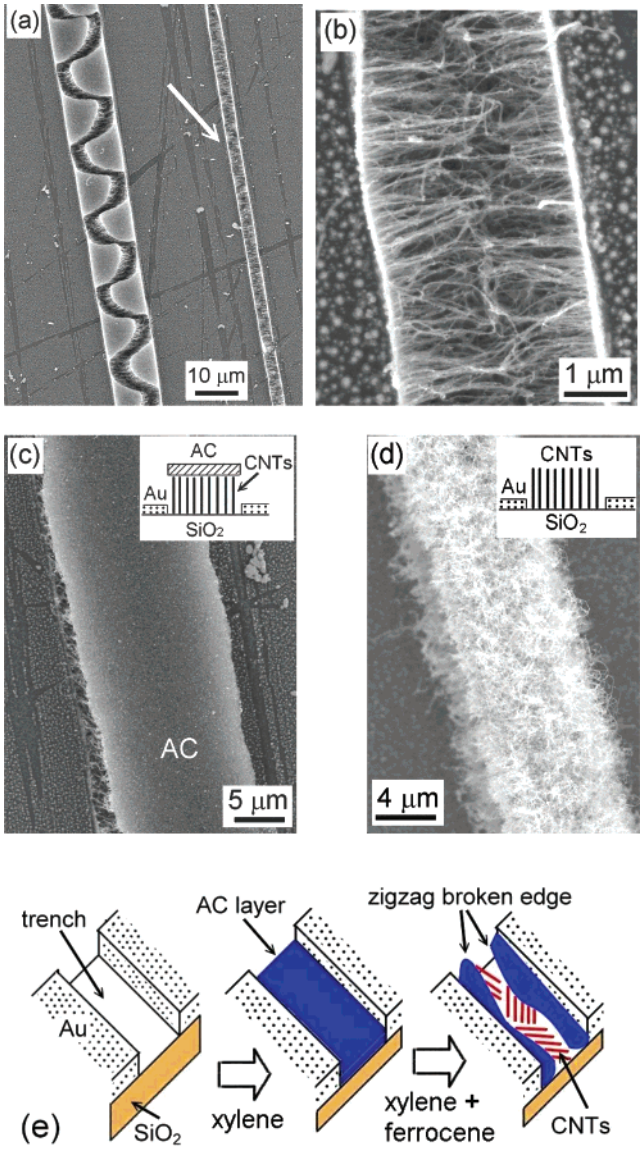

Figure 2. (a) SEM image of two Au trenches with zigzag patterns (the left 12 μm trench), and without zigzag trace (the right 3 μm trench; see the arrow). (b) Close view of the 3 μm trench shows aligned nanotubes grown inside, however, without pattern formation. (c) Aligned CNTs covered with a complete AC layer produced in a larger trench (16 μm wide), showing the disappearance of zigzag splitting. (d) A clean 10 μm CNT stripe without an AC layer on the top grown at reduced CVD temperature, showing no zigzag assembly. Insets in (c) and (d) are section view illustrations. (e) A proposed model for the deposition of an AC layer and subsequent split into zigzag patterns as the nanotube grows.

CNTs have an Fe particle sitting at the bottom of the tube (Figure 3b), consistent with a bottom-growth mechanism of nanotubes; carbon clusters add into the tube bottom (instead of top tip) to keep nanotubes growing, as illustrated in Figure 3c. Indeed, our previous study has shown that a large amount of γ-Fe particles located at the interface of SiO_2-CNTs is necessary for the formation of vertically aligned nanotubes.[12] This bottom-growth mechanism is further strengthened by the SEM study as shown in Figures 1 and 2: although the top tips of the CNTs were covered by an AC layer, the nanotube bottoms remained active to uptake the carbon source and hence could push upward the AC layer by continual CNT growth.

We found that, during the CNT growth, the AC layer on top of them was rotating correspondingly. Figure 4a−c shows SEM

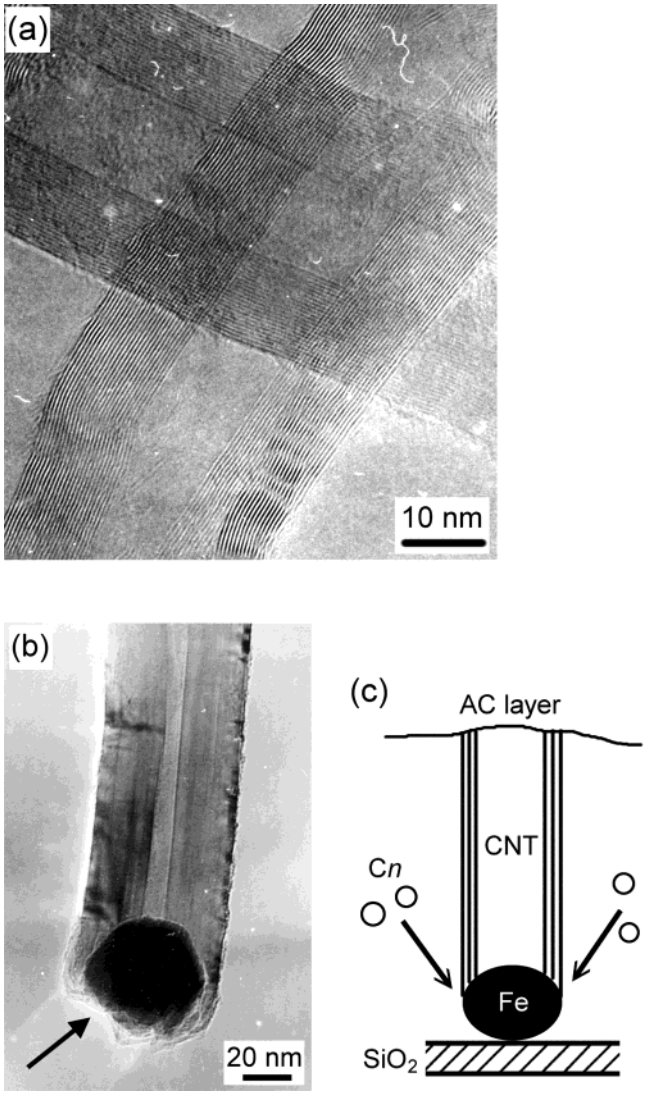

Figure 3. (a) TEM image of CNTs grown in Au trenches. (b) An Fe particle (see arrow) adhering to the nanotube bottom. (c) Illustration of the bottom growth of CNTs, in which carbon clusters (C_n) add to the catalyst sitting at the tube bottom.

images of zigzag patterns prepared by different CVD intervals of 2, 3, and 5 min, respectively, and therefore having an incremental nanotube length. We can see that the top AC layer rotates gradually from horizontal to a nearly vertical position as the underlying nanotubes grow longer (insets of Figure 4). The nanotubes at the broken site access directly the carbon source and hence grow much faster than others covered by the AC layer. The nonuniform growth rate of the nanotubes resulted in different tube lengths in the same trench. The nanotubes near the AC broken site became the longest, and consequently pushed the AC layer to rotate and gradually open toward the outside of the trench. At the same time, the orientation of the nanotubes changed from initially vertical to nearly 45° tilted upon the substrate surface, with the nanotube tips being stretched by the rotating AC layer (insets of Figure 4). Along the Au trench, all the zigzag patterns rotate at the same speed and hence show the same nanotube orientation and angular position of the AC layer (Figure 4d). The angle between the plane of the AC layer and the substrate normal ($\theta_{AC-normal}$) decreases linearly with increased CNT length (L_{CNT}), and shows a similar tendency for trenches with different widths, as plotted in Figure 5. Thus, we can derive the CNT length by monitoring the angular position of the AC layer. This controllable simultaneous motion of a

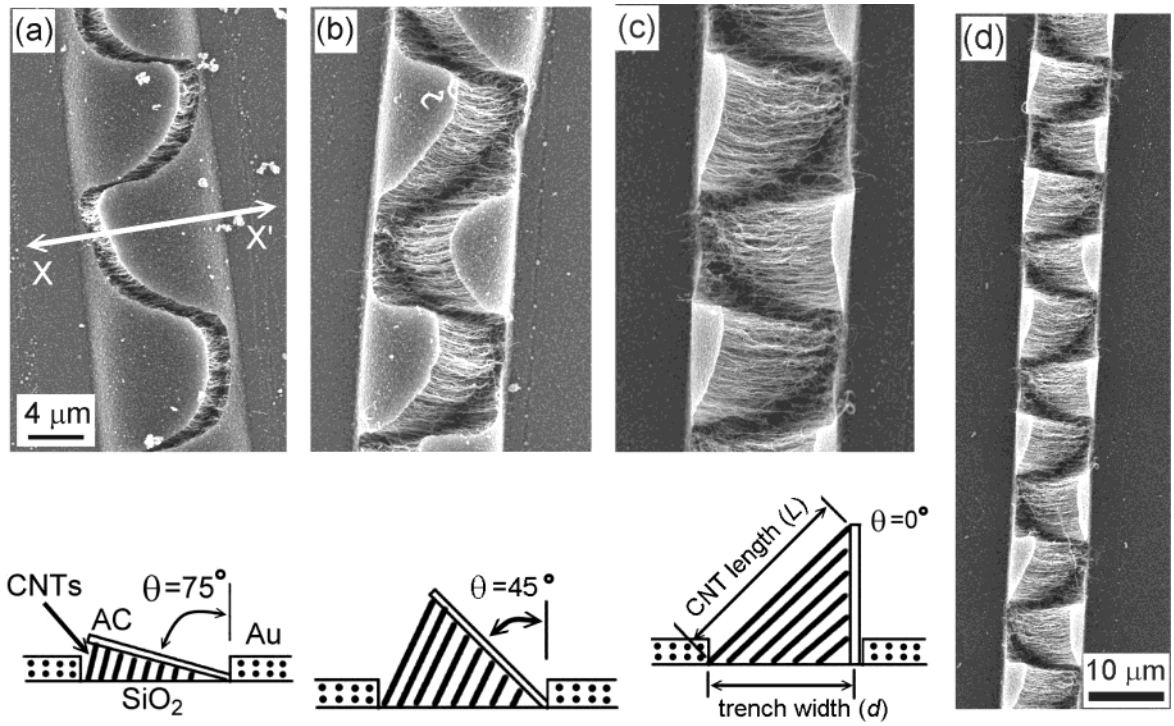

Figure 4. Zigzag CNT patterns grown in an 11 μm trench by different CVD intervals of (a) 2, (b) 3, and (c) 5 min. Illustrations in the insets show continuous rotation of the AC layer during nanotube growth (section view from the site labeled as XX′). (d) Two rows of zigzag patterns along a Au trench, showing uniform pattern distribution and simultaneous rotating motion.

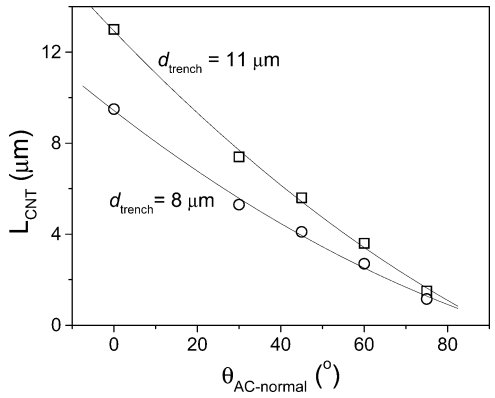

Figure 5. $\theta_{AC-normal}$ (as labeled in the Figure 3 insets) versus CNT length (L_{CNT}) for Au trenches with two different widths (8 and 11 μm).

row of CNT patterns is very useful for creating arrays of nanotube-based thermal sensors or rotational actuators.

Conclusions

In summary, we report self-assembly of zigzag CNT patterns inside Au microtrenches by producing an AC layer at elevated CVD temperature, which splits into two zigzag-edged pieces during nanotube growth. The zigzag patterns consist of aligned nanotubes with adjustable length and orientation, and the pattern size and interpattern distance are controlled by the size of the Au trenches. It might be interesting to further investigate the similar self-assembly process in trenches with various shapes (e.g. square, circular, triangular) and sizes to explore the possibility of formation of novel or even *irregular* CNT patterns, which otherwise would be difficult to design by conventional lithography. Our way provides a simple nonlithographical route for creating three-dimensional CNT structures consisting of nanotubes with multiple/tunable lengths and orientations.

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References and Notes

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