Patterned Growth of Vertically Aligned Carbon Nanotubes on Pre-patterned Iron/Silica Substrates Prepared by Sol−Gel and Shadow Masking

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The sol−gel technique has been used to prepare film-like iron/silica substrates for the large-scale growth of highly aligned carbon nanotubes. Here, we show that by using transmission electron microscopy (TEM) grids as shadow masks, the sol−gel technique can be readily adapted to prepare patterned film-like iron/silica substrates, on which various kinds of micropatterns of vertically aligned carbon nanotubes can be fabricated. Not only were micropatterns composed of regularly arranged nanotube towers of (when viewed from the top) squares and hexagons obtained, but also patterns consisting of complex tube features (for example, hollow tube-like towers and nanotube networks) were fabricated via our approach. The synthesis of these morphologies can be readily controlled by using TEM grids with different openings and by tuning the parameters in preparing the patterned substrates. In comparison with other techniques that involve sophisticated lithography, our technique represents a simple and low-cost approach to the micropatterning of aligned carbon nanotubes.

1. Introduction

The motivation for the preparation of micropatterns of vertically aligned carbon nanotubes was driven by the strong interest in their physical properties and potential applications (for example, as cold field emitters in panel displays).[1−4] Several methods have been successfully developed for fabricating micropatterns of nanotubes. Basically, the procedure involves the following three steps: (1) creating a micropattern on a substrate by photo- or electro-beam lithography,[5−8] soft-lithography,[9−11] or shadow masking;[12,13] (2) transporting catalysts to the desired position of the patterns through the vapor phase (for example, by evaporation[12] or sputtering[13] of transition metals) or by direct printing,[14] contact printing, [9−11,15] or spin coating[11] of solution-based catalyst precursors; and (3) growing carbon nanotubes on catalyst patterns via chemical vapor deposition of hydrocarbons (for example, acetylene,[10,15] ethylene,[12−14] or methane[11]), iron(II) phthalocyanine ($FeC_{32}N_8H_{16}$, FePc),[5,9] or a mixture of xylene/ferrocene [C_8H_{10}/$Fe(C_5H_5)_2$].[6] The combination of two or three of these steps results in the formation of nanotube patterns with different orientations and morphologies. For example, micropatterns of vertically aligned nanotube towers of (when viewed from the top) squares,[8,11−13] hexagons,[5] flowers,[6,10] and letters [9] have been successfully fabricated.

Among the methods mentioned above, the ones involving solution-based catalyst precursors have recently attracted much more attention due to their low cost (no need for expensive photo- or electro-lithography facilities), the advantages in easily tuning the composition and concentration of the catalysts, and the ability to form various complex configurations of catalyst patterns by adjusting the physical properties (such as surface free energy and viscosity) of the solution.[9−11,14,15] These features make it possible to investigate a new class of customer-designed catalysts, which allow better control of the diameters of the nanotubes, the density of the nanotubes in the patterns, and their orientation and morphology on the substrates. The main micropatterning technique that involves solution-based catalyst precursor is soft lithography,[9−11,15] which used a patterned elastomer fabricated from poly(dimethylsiloxane) (PDMS) as the mask, stamp, or mold. Because the elastomer can conform to and seal reversibly against the contours of a surface, it can be used as a mask or a stamp for the solution-based catalyst precursor. In contrast, a rigid metal shadow mask was believed to be impossibe to use to pattern materials from solution because of the air gap between the mask and the substrate.[15]

Using the sol−gel technique, the solution-based catalyst precursor containing tetraethoxysilane (TEOS) and iron nitrate has been cast into film-like iron/silica substrates for the large-scale growth of highly aligned arrays of multiwall carbon nanotubes.[16−18] The nanotubes synthesized by this method have a very high quality, uniform diameter distribution, and controllable lengths. In this article, we demonstrate that by using transmission electron microscopy (TEM) grids formed from rigid metals (such as copper and gold) as the shadow masks, the sol−gel technique can be readily adapted to prepare patterned film-like iron/silica substrates, so that regular micropatterns of vertically aligned carbon nanotubes can be obtained. In comparison with the methods reported previously, our technique represents a simple and low-cost approach to the micropatterning of aligned carbon nanotubes. More importantly, our approach can be readily used to fabricate various kinds of complex nanotube patterns (for example, hollow tube-like towers and nanotube networks), which are difficult to synthesize using a conventional lithography technique, by simply using TEM grids with different openings and by tuning the parameters in preparing the patterned substrates.

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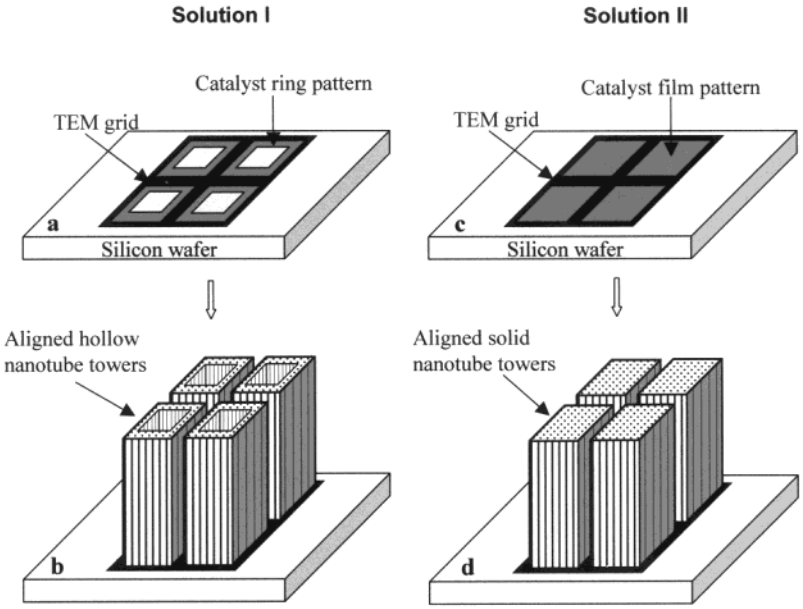

Figure 1. Schematic diagram of the ring-like (a) and uniform film-like (c) catalyst patterns formed inside the TEM grids with square openings by using Solution I and Solution II as the catalyst precursors, respectively. The ring-like catalyst pattern results in the formation of micropattern of hollow tube towers (b), while the uniform film-like catalyst pattern generates micropattern of solid tube towers (d).

2. Experimental Procedure

Materials and Reagents. Used in this study were $Fe(NO_3)_3 \cdot 9H_2O$ and TEOS from Alfa Aesar Inc.; ethanol from Sigma-Aldrich Corporation; Pluronic P-123 triblock copolymer from BASF Inc. (Mount Olive, NJ); N-doped silicon wafers ($\langle 100 \rangle$, 1−10 Ω cm) from Wafer World Inc. (West Palm Beach, FL); ultrahigh-purity nitrogen (99.999%) and hydrogen (99.999%) from Air Liquide Group; acetylene (99.6%) from Matheson Tri-Gas Inc.; and TEM grids from Ted Pella Inc. The silicon wafers were ultrasonically cleaned in ethanol before use.

Catalyst Solution Preparation. Two kinds of solution, Solution I and Solution II, were prepared. Solution I was prepared by mixing TEOS (3 mL), iron nitrate aqueous solution (1.5 M, 3 mL), and ethanol (10 mL) by means of magnetic stirring for 1 h. Solution II was prepared as follows. First, 0.8 g of Pluronic P-123 triblock copolymer was dissolved in 10 mL of ethanol. Next, 3 mL of TEOS and 3 mL of 1.5 M iron nitrate aqueous solution were added and stirred for 1 h. The addition of triblock copolymer improves the wetting ability of the solution with the silicon wafer and increases the viscosity of the solution, so that a very thin and uniform film can be coated on the surface of the silicon wafer by dip coating without cracking. Both solutions were used immediately.

Preparation of Catalyst Film and Patterns. Two kinds of film-like iron/silica substrates were prepared for nanotube growth: (1) thick film (with thickness of ∼30 to 50 μm) without patterning, and (2) thin film (with thickness of ∼1 μm) patterned with TEM grids. For the nonpatterned thick film, the solution was dropped onto the surface of the silicon wafer to form a film of solution with thickness of about 30 to 50 μm. After gelation, the gel was dried overnight at 80 °C to remove the excess water and solvent, during which time the film cracked into small pieces and detached from the wafer surface to form film-like free-standing substrates. This process is similar to that described in refs 16−18.

For the patterned thin film, the solution was coated on silicon wafers by dip coating to form a very thin film of solution. When the film was still in the liquid state, copper or gold TEM grids with square, hexagon, or other kinds of openings were placed on the film to act as a shadow mask. During the process of gelation, Solution I tended to break down in each opening of the TEM grid because of the development of holes in the film, resulting in the formation of a ring-like solid catalyst film along the edge of each opening (Figure 1a). For Solution II, however, a stable and uniform solid film was formed in each hole of the grid after gelation (Figure 1c), due to the effect of triblock copolymer. The patterned substrates were also dried overnight at 80 °C. Before the patterned substrates were loaded into a tube furnace to grow the nanotubes, some grids were removed from the patterns so that the influence of the grids on the nanotube growth and the quality of the patterns could be evaluated.

Calcination, Reduction, and Nanotube Growth. The film-like and patterned substrates were loaded into a tube furnace (Lindbergh Blue) and calcinated at 450 °C for 10 h under vacuum condition (∼2×10^{-3} Torr), followed by reduction at 600 °C for 5 h in hydrogen atmosphere. At this stage, large quantities of iron/silica nanoparticles formed on the film surfaces, acting as catalysts for nanotube growth.[17,18] Finally, a flow of ∼10% acetylene in nitrogen was introduced into the reaction chamber at a flow rate of 100 mL/min, and aligned and/or patterned nanotubes were synthesized on the substrates at 700 °C and 180 Torr. The reaction time varied between 1 and 5 h.

Microscopy Characterization. The as-synthesized nanotube arrays and micropatterns were examined by a Philips XL-30 field emission scanning electron microscope (SEM) operated at 10 kV. The microstructures of the nanotubes were investigated with a Philips CM200 high-resolution TEM (HRTEM) operating at 200 kV.

3. Results and Discussion

The substrates prepared with and without triblock copolymer exhibit the same catalytic activity for nanotube growth. The nanotubes always grow along the substrate surface normal to form arrays (for the nonpatterned substrates) or micropatterns (for the patterned substrates) of highly aligned nanotubes. For the patterned substrates, not only were micropatterns of regularly

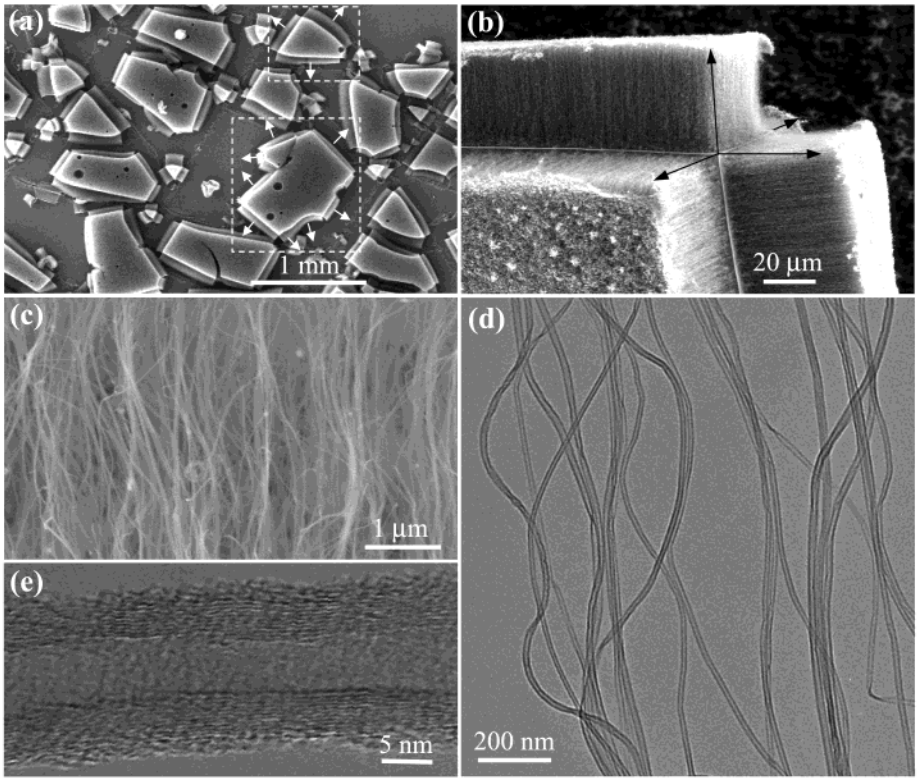

Figure 2. SEM and TEM images of aligned carbon nanotubes grown on film-like iron/silica substrates. (a) Low-magnification SEM image of about 20 pieces of film-like substrates covered with aligned carbon nanotube arrays. The white arrowheads around the two substrates represent the growth direction of the nanotubes from the side surfaces of the substrates. (b) A close-up view of a substrate corner, showing aligned nanotubes growing out perpendicularly from four adjacent surfaces of the corner. The growth direction of the nanotubes on each surface is indicated by a black arrow. (c) High-magnification SEM image of the nanotube arrays, showing highly aligned and well-separated carbon nanotubes. (d) TEM image of a bundle of aligned carbon nanotubes. (e) HRTEM image of a carbon nanotube, showing well-ordered graphitic lattice fringes.

aligned towers of squares and hexagons prepared but so also were patterns of complex configurations that were difficult to achieve by other techniques prepared. In the following, we first describe the nanotube arrays formed on the film-like free-standing substrates to show some common SEM and TEM features that also occur on the tube arrays formed on the patterned substrates, and then focus on the micropatterns of aligned nanotube towers with various kinds of configurations.

3.1. Nanotubes Grown on Film-like Free-Standing Substrates. During the growth process, the carbon atom can homogeneously be deposited onto all substrate surfaces, including the lower surface that contacts the supporting silicon wafer. As a result, the nanotubes grew out perpendicularly from all substrate surfaces to form aligned nanotube arrays with the same density and length. The substrates were finally lifted from the surface of the silicon wafer by the nanotube arrays formed on the lower surfaces. Figure 2a is a low-magnification SEM image of about 20 pieces of film-like substrates covered with carbon nanotube arrays. The contrast between the nanotube arrays formed on the top and side surfaces of the substrates is clearly seen. Regardless of the shape of the substrates, the nanotube arrays are always perpendicular to the surfaces from which they grow, as the white arrowheads surrounding the side surfaces of two substrates in Figure 2a indicate. This growth feature is clearly displayed in Figure 2b, which shows the nanotube arrays growing out perpendicularly from the four adjacent surfaces of a substrate corner. The edge of the substrate is very clear, and the angle between two adjacent arrays is about 90°. Figure 2b also shows that the nanotube arrays grown on different surfaces have the same length and nanotube density. High-magnification SEM examinations show that the nanotubes are vertical to the substrate surface and remain aligned as their length increases (Figure 2c). The length of the nanotube arrays increases with the period of growth at a rate of $\sim$15 μm/h.

Figure 2d is a TEM image of a bundle of aligned nanotubes, showing that the nanotubes are of uniform diameter, with outer and inner diameters in the range of 20 to 30 nm and 5 to 10 nm, respectively. No catalyst particles were observed inside the nanotubes. HRTEM studies show that the nanotubes are well graphitized and typically consist of 10 to 30 concentric graphite layers (Figure 2e). An amorphous carbon layer with thickness of around 1 nm usually coated the outer surface of the tubes as a result of the low growth temperature (700 °C) employed in our experiment. The formation of the amorphous carbon layer may be circumvented by growth of the nanotubes at a higher temperature (>1000 °C). However, our experiments show that the sol−gel prepared substrates can only withstand temperature of $\sim$800 °C, above which the substrates will be cracked and thus lose the catalytic effect for aligned nanotube growth. In addition, in the case of growing nanotube patterns by using TEM grids as the masks, the grids will deform and detach from the silicon wafer surface at higher temperature, losing their confinement effect in growing regular and well-defined micropatterns of aligned nanotube towers.

3.2. Micropatterns of Aligned Carbon Nanotubes. For the catalyst patterns prepared from Solution II (with copolymer), uniform catalyst films formed in all openings of the TEM grids (Figure 1c). On the other hand, for the patterns prepared from Solution I (without copolymer), a ring-like catalyst film was usually formed along the edge of each opening of the grid (Figure 1a). These two kinds of catalyst film configurations will result in the formation of two kinds of micropatterns of nanotube

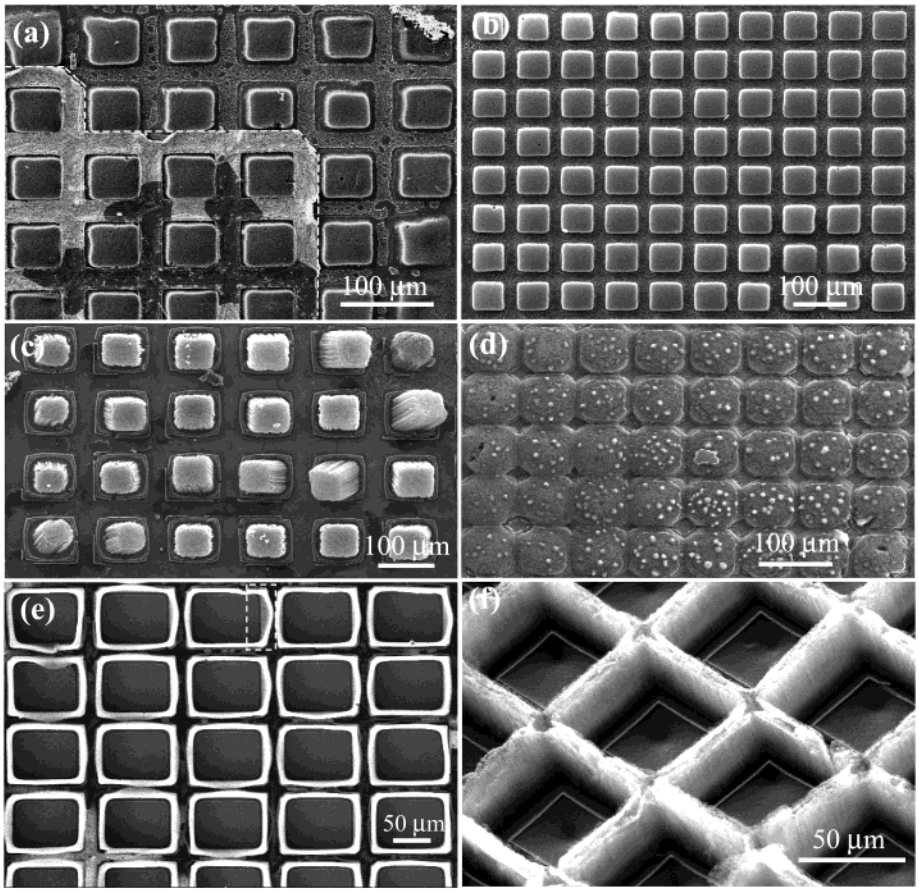

Figure 3. SEM images of nanotube micropatterns formed by using TEM grids with square opening as the masks. Micropatterns of regularly arranged square towers obtained by using (a) a 300 mesh gold grid after 2 h of growth, (b) a 300 mesh copper grid after 1 h of growth, and (c) a 200 mesh copper grid after 4 h of growth. Part of the grid in (a) remains for imaging, and the boundary between the covered part (lower left) and uncovered part (upper right) is indicated by a white dashed line. (d) An ambiguous pattern grown without the presence of a TEM grid during carbon deposition. The substrates corresponding to images a−d were prepared by using Solution II (with copolymer) as the catalyst precursor. (e) Micropatterns of rectangular-like rings consisting of perpendicularly aligned carbon nanotubes. The wall of the ring is clearly shown in the boxed region. The corresponding substrate was prepared by using a 200 mesh grid with rectangular openings. (f) A nanotube network grown along a catalyst network that initially existed under the bar of a TEM grid. The grid was removed before carbon deposition. The substrates corresponding to images e−f were prepared by using Solution I (without copolymer) as the catalyst precursor.

towers (i.e., solid towers (Figure 1d) for the uniform film and hollow towers (Figure 1b) for the ring-like film). However, both kinds of films have the same activity for nanotube growth as the free-standing thick films described in Section 3.1, for example, the growth direction, density, diameter distribution, and microstructure of the nanotubes. In addition, as will be described below, whether the TEM grids remain in place during carbon deposition also influences the morphology of the patterns.

TEM Grids with Square Openings as Shadow Masks. When the TEM grids remain in place during carbon deposition, the aligned carbon nanotubes grow outward only from the open holes in the grid, forming a regular micropattern of aligned nanotube towers. Shown in Figure 3a is a SEM image of an aligned nanotube pattern produced by using a 300 mesh gold TEM grid consisting of square windows as the mask and Solution II as the catalyst precursor. To provide a better understanding of the shadow effect of the grid, part of the grid was retained for SEM imaging. The white dashed line in Figure 3a is the boundary between the parts with (i.e., lower left) and without (i.e., upper right) the TEM grid. It is clear that the nanotube towers fit the grid windows very well. Examination of the edge region of the towers confirms that the boundary between the deposited and masked areas is well defined and preserved. Thus, the spatial resolution of the patterns is well controlled by the resolution of the mask used. Figure 3b shows another example of a nanotube pattern obtained by using a 300 mesh copper grid as the mask, in which a highly regular array of 80 square nanotube towers with the same size and pitch distance is displayed. While the cross-section of the nanotube towers is controlled by the structure of the mask, the height of the towers is controlled by the growth duration, as evidenced by comparison of the pattern in Figure 3c (after 4 h of growth) with those in Figure 3a (after 2 h of growth) and in Figure 3b (after 1 h of growth). As the height of the towers increases, the towers tend to tilt away from the substrate surface normal (Figure 3c). The patterns of the nanotube towers in Figure 3a−c are similar to those obtained by others,[8,12] who used complicated fabrication procedures and expensive lithography and/or electron-beam evaporation facilities in the preparation of the catalyst patterns. In our approach, however, the fabrication procedure is simple and no sophisticated facility was used. High-magnification SEM and TEM analyses of the nanotube towers show results similar to the aligned nanotube arrays shown in Figure 2c−e.

For the patterns shown in Figure 3a−c, the TEM grids remained on the silicon wafer surface during carbon deposition. Thus, the growth of the nanotubes from the catalyst film under the grid bar was prevented. If the grid is removed before carbon deposition, however, the nanotubes grow out from not only the window part but also the bar part of the grid, resulting in the

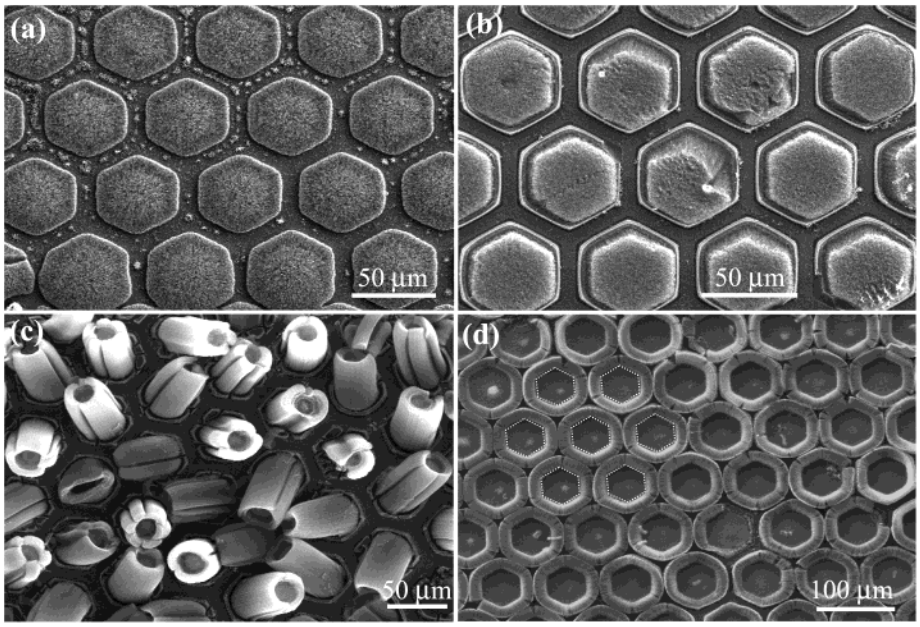

Figure 4. SEM images of nanotube micropatterns formed by using TEM grids with hexagonal opening as the masks. Micropatterns of regularly arranged hexagonal towers obtained by using 300 mesh copper beehive grids after (a) 1 h and (b) 2.5 h of growth. The substrates corresponding to images a,b were prepared by using Solution II (with copolymer) as the catalyst precursor. (c) Micropattern of hierarchically ordered carbon tubes obtained by using a 400 mesh copper beehive grid as the shadow mask. (d) A "nanotube grid" consisting of hexagonal windows, which replicates the structure of a 300 mesh copper beehive grid after 2 h of carbon deposition. The grid was absent during nanotube growth. The substrates corresponding to images c−d were prepared by using Solution I (without copolymer) as the catalyst precursor.

formation of an ambiguous pattern, as shown in Figure 3d. This result suggests that keeping the TEM grids in place during carbon deposition is conducive to obtaining a clear pattern of regularly aligned nanotube towers, at least for the substrates prepared by using Solution II as the catalyst precursor.

The chemical composition and physical properties (such as surface free energy and viscosity) of the catalyst solution influence the uniformity and morphology of the final catalyst patterns. Using Solution II, we can obtain a uniform catalyst pattern inside the grid (Figure 1c) and micropatterns of regularly arranged nanotube towers (as shown in Figure 3a−c) can be readily synthesized. For Solution I, however, the solution tends to distribute itself along the edge of the mask window, forming micropatterns of catalyst rings (Figure 1a). Chemical vapor deposition of acetylene over this kind of catalyst pattern results in the formation of a micropattern of hollow nanotube towers, with walls consisting of vertically aligned nanotubes, as shown in Figure 3e. The catalyst pattern corresponding to Figure 3e was prepared by using a 200 mesh copper TEM grid with rectangular openings as the mask. If the TEM grid is removed before nanotube growth, a nanotube network is formed along the trace of the TEM grid bars (Figure 3f), which replicates the structure of the original TEM grid very well. The constituent nanotubes in the network are aligned normal to the substrate surface.

TEM Grids with Hexagonal Openings as Shadow Masks. Under the same conditions of substrate preparation and nanotube growth, the TEM grids consisting of hexagonal windows exhibit the same behavior as the grids with square windows in the micropatterning of aligned carbon nanotubes. Figure 4 shows four typical SEM images of nanotube micropatterns grown on catalyst patterns prepared by using TEM grids with hexagonal windows as the masks. The catalyst patterns corresponding to the nanotube patterns in Figure 4a,b were prepared by using Solution II as the catalyst precursor. It is clear that regularly arranged micropatterns of hexagonal nanotube towers were obtained in both cases, indicating that uniform catalyst films were formed inside the windows of the grids. The height of the towers increases with the growth time, as evidenced by comparison of Figure 4a (after 1 h of growth) with Figure 4b (after 2.5 h of growth).

Ring-like catalyst patterns were also formed inside the hexagonal windows of the grids when Solution I was used as the catalyst precursor. As a result, micropatterns of hierarchically ordered carbon tubes[19] (i.e., ordered microtubes composed of aligned carbon nanotubes) were obtained (Figure 4c). High-magnification SEM studies reveal that the wall of the large tube is composed of highly aligned carbon nanotubes, with the growth direction and axes of the nanotubes parallel to those of the microtubes. The detailed structures of the hierarchically ordered carbon tubes are given in ref 19. If the copper TEM grid is removed before nanotube growth, a same-size "nanotube grid" consisting of hexagonal windows will be well replicated after carbon deposition, as shown in the example of a 300 mesh "nanotube grid" in Figure 4d. The windows of the "nanotube grid" were constructed by aligned carbon nanotubes.

TEM Grids with Other Kinds of Openings as Shadow Masks. In addition to creating the patterns of regularly arranged square and hexagonal nanotube towers, our approach can also be used to prepare other kinds of nanotube features, for example, letters (Figure 5a,b), Arabic numerals (Figure 5c), and other complex patterns (not shown here), by using grids with related openings. Similar to the patterns described above, the constituent nanotubes in these letters and Arabic numerals are aligned normal to the substrate surface.

Discussion. The combination of sol−gel technique and shadow masking provides a simple, low-cost, and versatile approach to the patterning of substrates for the growth of micropatterns of aligned carbon nanotubes. By using the patterned substrates prepared by this combined approach, we can grow nanotube patterns with a variety of morphologies and configurations. Not only were micropatterns of regularly aligned towers of squares (Figure 3a−c) and hexagons (Figure 4a,b)

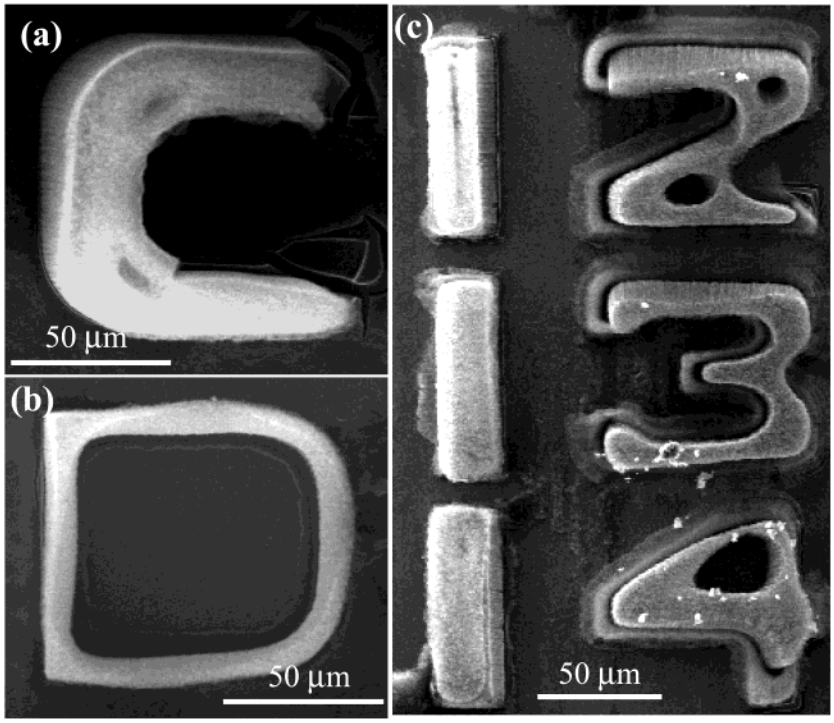

Figure 5. SEM images of (a and b) letters and (c) Arabic numerals consisting of vertically aligned carbon nanotubes. The substrates corresponding to these images were prepared by using TEM grids with openings shaped like letters and Arabic numerals as the shadow masks and Solution II (with copolymer) as the catalyst precursor.

prepared, but also the patterns with complex morphologies, for example, hollow towers (Figure 3e), hierarchical structures (Figure 4c), and nanotube networks (Figures 3f and 4d), which are difficult to achieve by other techniques, were obtained. The formation of the various kinds of nanotube patterns is directly related to the features of the catalyst patterns, which were determined by many factors. These factors include the following:[14,15,20,21] the chemical composition and physical properties (such as surface free energy and viscosity) of the solution; the surface condition (such as hydrophobic or hydrophilic) of the silicon wafer; the thickness of the dip-coated solution film on the silicon wafer, the difference in surface free energy among the solution film, silicon wafer, and grids; and the capillary interactions between the solution and grids. The influences of some of these factors have been observed by others in the direct printing[14] or contact printing[11,15,20] of solution-based catalyst precursors for the patterned growth of aligned carbon nanotubes. In our experiments we found that the following three factors are critical for the controlled synthesis of various kinds of nanotube patterns. First, the addition of copolymer helps to form a uniform catalyst film inside the TEM grids, so that micropatterns of solid nanotube towers (as shown in Figures 3a−c and 4a,b) can be obtained. Without the copolymer, ring-like catalyst patterns tend to form along the edges of the grid openings, resulting in the formation of patterns of hollow nanotube towers, as shown in Figures 3e and 4c. Second, the thickness of the solution film should be controlled to be ~1 μm. If the film is too thin, the TEM grids cannot stick firmly to the silicon wafer, losing their effect in patterning the substrate. If the film is too thick, the solution will overflow the grids; again, the patterned substrate cannot be obtained. In addition, it is hard to get ring-like catalyst patterns when using Solution I if the thickness of the solution is much over 1 μm. Third, keeping grids in place during carbon deposition is conducive to obtaining a clear pattern of regularly aligned nanotube towers. If the grids are absent during nanotube growth, however, some interesting patterns of nanotube networks, as shown in Figures 3f and 4d, can be synthesized for the substrate prepared using Solution I as the catalyst precursor.

4. Conclusion

A simple and effective approach based on sol−gel technique and shadow masking was developed to prepare patterned iron/silica substrates for the growth of micropatterns of aligned carbon nanotubes. Our approach involves the dip coating of a solution containing TEOS, iron nitrate, water, and ethanol onto a silicon wafer, using TEM grids with various kinds of openings as the shadow masks to obtain patterned substrates, and chemical vapor deposition synthesis. Micropatterns of regularly arranged nanotube towers with shapes (when viewed from the top) of squares, hexagons, rings, networks, letters, and Arabic numerals were successfully fabricated. The synthesis of these morphologies can be readily controlled by using TEM grids with different openings and by tuning the parameters in preparing the patterned substrates. Because no sophisticated facilities such as lithography were involved in preparing the catalyst patterns, our technique represents a simple, low-cost approach to the micropatterning of aligned carbon nanotubes. These low-cost nanotube micropatterns might find application in the area of flat panel displays.

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References and Notes

(1) De Heer, W. A.; Châtelain, A.; Ugarte, D. *Science* **1995**, *270*, 1179.

(2) Rinzler, A. G.; Hafner, J. H.; Nikolaev, P.; Lou, L.; Kim, S. G.; Tománek, D.; Nordlander, P.; Colbert, D. T.; Smalley, R. E. *Science* **1995**, *269*, 1550.
(3) Collins, P. G.; Zettl, A. *Appl. Phys. Lett.* **1996**, 69, 1969.
(4) Che, G.; Lakshmi, B. B.; Fisher, E. R.; Martin, C. R. *Nature* **1998**, *393*, 346.
(5) Yang, Y. Y.; Huang, S. M.; He, H. Z.; Mau, A. W. H.; Dai, L. M. *J. Am. Chem. Soc.* **1999**, *121*, 10832.
(6) Wei, B. Q.; Vajtai, R.; Jung, Y.; Ward, J.; Zhang, R.; Ramanath, G.; Ajayan, P. M. *Nature* **2002**, *416*, 495.
(7) Bae, E. J.; Choi, W. B.; Jeong, K. S.; Chu, J. U.; Park, G. S.; Song, S.; Yoo, I. K. *Adv. Mater.* **2002**, *14*, 277.
(8) Sohn, J. I.; Lee, S. H. *Appl. Phys. A* **2002**, *74*, 287.
(9) Huang, S. M.; Mau, A. M. H.; Turney, T. W.; White, P. A.; Dai, L. M. *J. Phys. Chem. B* **2000**, *104*, 2193.
(10) Zheng, G. F.; Zhu, H. G.; Luo, Q.; Zhou, Y. M.; Zhao, D. Y. *Chem. Mater.* **2001**, *13*, 2240.
(11) Ng, H. T.; Foo, M. L.; Fang, A. P.; Li, J.; Xu, G. Q.; Jaenicke, S.; Chan, L.; Li, S. F. Y. *Langmuir* **2002**, *18*, 1.
(12) Fan, S. S.; Chapline, M. G.; Franklin, N. R.; Tombler, T. W.; Cassell, A. M.; Dai, H. J. *Science* **1999**, *283*, 512.
(13) Delzeit, L.; Nguyen, C. V.; Chen, B.; Steven, R.; Cassell, A.; Han, J.; Meyyappan, M. *J. Phys. Chem. B* **2002**, *106*, 5629.
(14) Cassell, A. M.; Verma, S.; Delzeit, L.; Meyyappan, M.; Han, J. *Langmuir* **2001**, *17*, 260.
(15) Kind, H.; Bonard, J.; Forró, L.; Nilsson, L.; Schlapbach, L. *Langmuir* **2000**, *16*, 6877.
(16) Li, W. Z.; Xie, S. S.; Qian, L. X.; Chang, B. H.; Zhou, B. S.; Zhou, W. Y.; Zhao, R. A.; Wang, G. *Science* **1996**, *274*, 1701.
(17) Pan, Z. W.; Xie, S. S.; Chang, B. H.; Wang, C. Y.; Lu, L.; Liu, W.; Zhou, W. Y.; Li, W. Z.; Qian, L. X. *Nature* **1998**, *394*, 631.
(18) Pan, Z. W.; Xie, S. S.; Chang, B. H.; Sun, L. F.; Wang, G. *Chem. Phys. Lett.* **1999**, *299*, 97.
(19) Pan, Z. W.; Zhu, H. G.; Zhang, Z. T.; Im, H. J.; Dai, S.; Beach, D. B.; Lowndes, D. H. *Chem. Phys. Lett.*, submitted.
(20) Carré, A.; Eustache, F. *Langmuir* **2000**, *16*, 2936.
(21) Bowden, N. B.; Weck, M.; Choi, I. S.; Whitesides, G. M. *Acc. Chem. Res.* **2001**, *34*, 231.