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Grow Single-Walled Carbon Nanotubes Cross-Bar in One Batch

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Large area, well-aligned single-walled carbon nanotubes (SWNTs) with node density up to 10^7/cm^2 are prepared by a convenient one-step process, which is based on the two growth modes of carbon nanotubes: gas flow-directed growth mode and lattice-orientated growth mode. Carbon nanotubes cross-bar is realized by chemical vapor deposition approach where the direction of gas flow and the direction of lattice of the substrate (quartz) are perpendicular. Catalyst-pattern technique is applied to produce shipshape cross-bar structure, and optimum condition (especially growth temperature) for the process is carefully studied. Interaction between catalyst and substrate is identified as a critical factor for fabrication of SWNTs cross-bar for such interaction affects the length of lattice-orientated carbon nanotubes as well as the density of gas flow-directed carbon nanotubes. This growth phenomenon offers a capability to control the formation of the cross-bar structure.

SWNTs cross-bar has been regarded as a good candidate for nanoelectronic devices integration.[1] It has been proposed that carbon nanotubes cross-bar can be integrated into nonvolatile random access memory for molecular computing.[2] Several efforts have been developed for fabricating such cross-bar structure, including carbon nanotubes transfer technique[3] and self-assembly.[4] However, these kinds of method always involve further solution treatment or etching process that inevitably affects the property of carbon nanotubes.[5] SWNTs cross-bar also can be obtained by a two step gas flow-directed growth,[6] which is more time-consuming and costly, and node density of cross-bar prepared by such method is low as well.

We report herein a rational approach to grow single-walled carbon nanotubes (SWNTs) cross-bar structures in one batch. The one batch approach is straightforward and avoids the need for post-treatment, thus we can get pristine SWNTs cross-bar to study its electrical properties. This process combines the two widely utilized growth modes for growing aligned SWNT arrays on surface: gas flow-directed growth mode (kite-mechanism)[6] and lattice-orientated growth mode.[7] Figure 1a illustrates the procedure of this approach. Lattice-orientated growth of SWNTs is along specific crystalline direction of lattice and is formed right on the substrate,[8] while gas flow-directed growth of SWNTs is along the direction of the gas flow and is formed micrometers above the substrate,[9] thus the two modes do not interfere with each other. By exploiting the compatibility of these two growth modes in a one growth process, SWNTs with cross-bar density up to 10^7 grids per square centimeter can be realized on quartz surface using patterned catalysts where the direction of gas flow and lattice are perpendicular to each other. A representative result is shown in Figure 1b.

Single crystal ST-cut quartz wafer is used as the substrate in this approach. On this surface, well-aligned high-density SWNT arrays can be grown, and the tube density can reach tens of tubes per micrometer.[10] $CuCl_2$/polyvinylpyrrolidone (PVP) alcohol solution and ferric hydroxide colloidal ethanol solution are used as catalyst precursors in different experiments respectively.

For growing SWNT cross-bar, two perpendicular strips of catalysts are patterned on quartz substrate and the catalyst-pattern procedure is shown in Figure 2. Briefly, after the quartz wafer is annealed at 900 °C for 8 h, a layer of PMMA is spun on it for electron beam lithography (EBL). Afterward, catalysts are deposited in those regions. The prepared substrate is then placed in the chemical vapor deposition (CVD) furnace at the direction in which lattice orientation and gas flow direction are perpendicular to each other. Through a 10 min reduction by hydrogen (100 sccm) and a 20 min growth at 930 °C where ethanol, bubbled by argon (10 sccm), is used as carbon resource, we obtain the SWNTs cross-bar as shown in Figure 1b.

Typical results of well-aligned SWNTs arrays along the lattice of quartz with length up to hundreds of micrometers and ultralong well-aligned gas flow-directed SWNTs are shown in Figure 3a,b, respectively. By combining these two growth modes, the SWNTs cross-bar with high grid density can be grown. The results are shown in Figures 1b and 3c. The average length of lattice-orientated SWNTs can reach hundreds of micrometers, and the distance between the nanotubes is about several micrometers. Gas flow-directed SWNTs are millimeters long and the distance between tubes can be reduced to about

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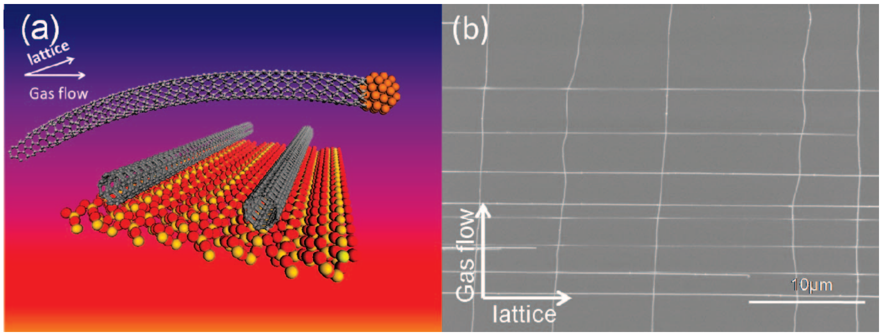

Figure 1. (a) Illustration of the mechanism for the growth of cross-bar structured carbon nanotubes. (b) High-magnification SEM image of carbon nanotubes cross-bar structure.

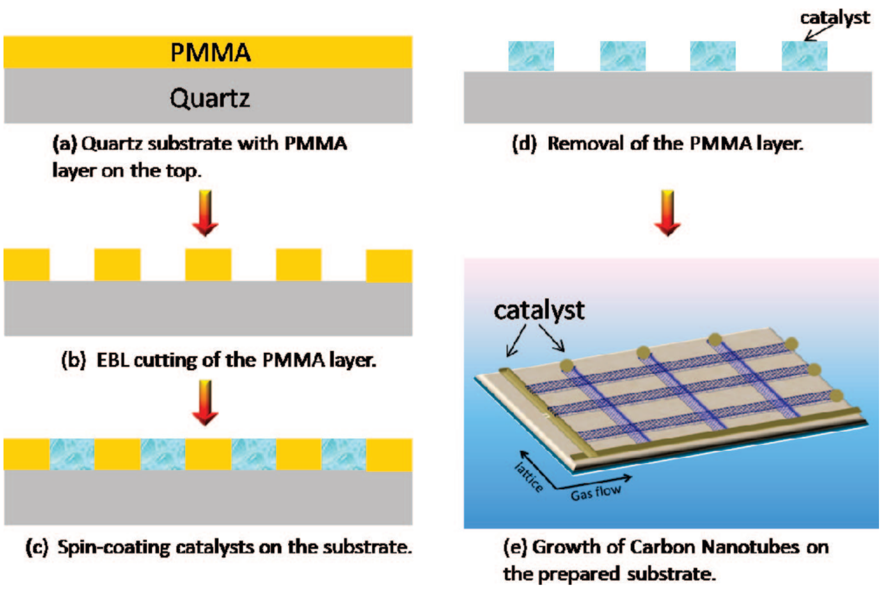

Figure 2. Schematic diagrams of preparation of the catalyst pattern and growth of carbon nanotubes cross-bar.

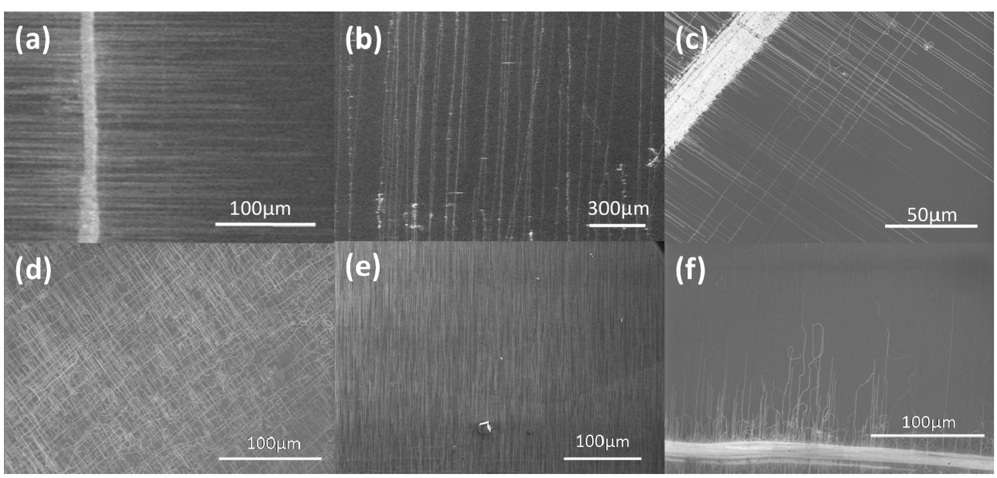

Figure 3. (a−c) Results of lattice-orientated, gas flow-directed, and both mechanisms controlled growth of carbon nanotubes respectively. (d) Cross-bar structured carbon nanotubes obtained by spin-coating catalysts on the substrate. Results of SWNTs grown at 900 and 970 °C are shown in (e,f).

10 μm. Thus large area, band-shaped, well-aligned SWNTs cross-bar with high node density can be acquired by our approach. SWNTs cross-bar can also be obtained by just spin-coating catalysts everywhere on the substrate, but the cross-bar structure is very irregular (shown in Figure 3d). Therefore the site-specific catalysts pattern is indispensable for obtaining well-defined cross-bars. In order to grow such structures at a large scale, two factors should be taken into consideration besides the catalyst pattern: growth temperature and interaction between catalyst and substrates.

Temperature is the most critical factor for the growth of SWNTs, especially for growth of SWNTs cross-bar by combining the two growth modes. The optimal conditions for lattice-orientated growth of SWNTs may be disadvantageous for the gas flow-directed growth and vice versa. Figure 3e shows that high density SWNT arrays along the lattice can be grown when

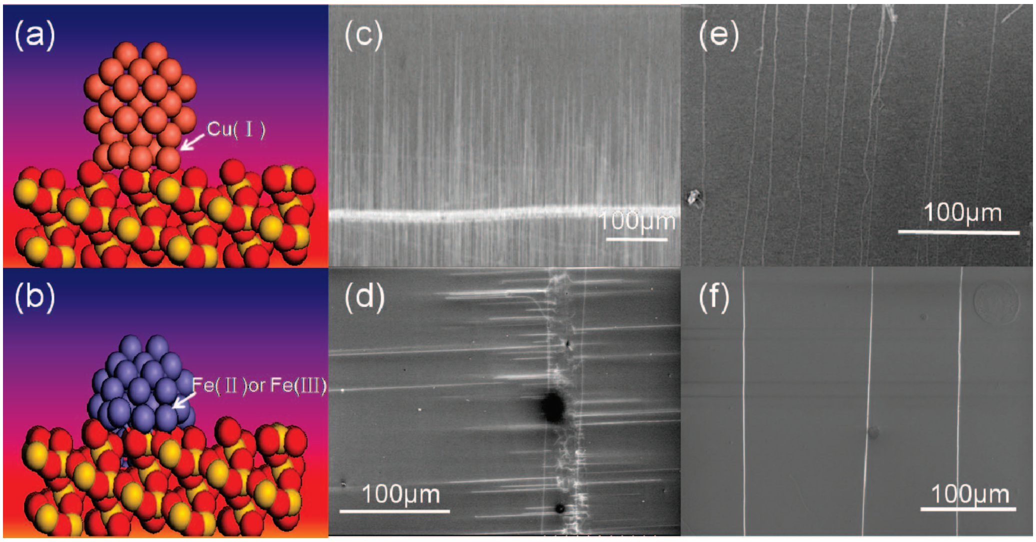

Figure 4. (a,b) The interaction between Cu, Fe nanoparticles and surface of quartz; the red balls represent oxygen atoms. (c,d) High-magnification SEM image of the lattice-assisted SWNTs catalyzed by Cu and Fe. (e,f) Results of gas flow-directed growth of carbon nanotubes where Cu and Fe are used as catalysts, respectively.

the growth temperature is 900 °C. However, such low temperature does not favor gas flow-directed growth of SWNTs and only a few gas flow-directed SWNTs were observed. As temperature rises, the density of lattice-orientated SWNTs decreases whereas the number of gas flow-directed SWNTs increases, so there is a tradeoff between the two modes. Moreover, when temperature reaches 970 °C, lattice is damaged after a long duration at such high temperature and leads to the growth of tortuous SWNTs as shown in Figure 3f. Considering these facts, we choose temperature ranges from 930 to 950 °C as the growth temperature; this is favorable for both growth modes, and the typical nanotube densities are shown in Figure 1b.

Interaction between catalysts and substrate is another important factor for the growth of SWNTs cross-bar. Normally, the length of lattice-orientated SWNTs is about tens of micrometers to a hundred micrometers,[11] which limits the probability to obtain large area SWNTs cross-bar. To grow long lattice-orientated SWNTs, we have investigated the growth of SWNTs catalyzed by Fe and Cu and have found that the interaction of Fe-SiO_2 is stronger than that of Cu-SiO_2, which leads to different growth results between the two catalysts. When temperature is increased to a certain degree, metal particles begin to diffuse over the substrate. Each catalyst-substrate pair has its peculiar diffusing temperature, which is an indicator of the interaction between substrate and catalysts: higher diffusing temperature means stronger interaction. It has been reported that Cu nanoparticles begin to diffuse on SiO_2 when temperature reaches about 625 K.[12] In experiments, when growing time reaches 40 min where Cu is used as catalyst, diffusion of Cu nanoparticles on quartz is observed clearly and the growth result is just like Figure 3d, while there is no obvious diffusion of Fe in the same condition. Thus we can say that the interaction between Fe and quartz is stronger than the interaction between Cu and quartz; this conclusion is also supported by computing results.[13]

To better understand these results, we study the nature of interaction between Cu, Fe, and quartz. It has been reported that the interaction between Cu nanoparticles and V_2O_3 is due to the charge transfer from Cu to V_2O_3 substrate and the following Cu−O bonding formed by hybridization of the Cu(I) 3d orbital with the nonbonding O 2p orbital of V_2O_3 surface.[14] We believe that similar charge-transfer interaction has occurred in our system. When Fe or Cu attaches to quartz, there is a charge transfer from the metal to the substrate, followed by bonding of cations and O atoms of SiO_2 surface. Cu cations are in the form of Cu(I) (Figure 4a) while Fe cations are in the form of Fe(II) or Fe(III) (Figure 4b). Because of the higher valence of Fe and based on HSAB (hard and soft acids and bases) theory,[15] we can deduce that Fe−O bonding is much stronger, thus interaction between Fe and quartz is much stronger than Cu-quartz interaction. By comparing the growth results of SWNTs catalyzed by Fe and Cu, we find that the average length of lattice assisted carbon nanotubes catalyzed by Cu can reach hundreds of micrometers, as shown in Figure 4c, while average length of carbon nanotubes catalyzed by Fe is less than 100 μm, which is shown in Figure 4d. Moreover, gas flow-directed carbon nanotubes catalyzed by Cu nanoparticles are much denser than those catalyzed by Fe (comparing Figure 4e,f). For lattice-orientated growth of carbon nanotubes, interaction of catalysts and substrate introduces friction between them when catalysts move on the substrate. Since the catalyst is at the top of carbon nanotubes,[16] based on tip-growth mechanism, such friction lowers the growth rate of lattice-orientated carbon nanotubes by retarding the movement of catalysts and finally leads to the termination of growth. So the stronger Fe-quartz interaction results in greater catalyst-substrate friction, which leads to shorter lattice-orientated carbon nanotubes compared to Cu in the same growth condition. Base-growth mechanism for lattice-orientated growth should also be taken into consideration here because there is strong evidence for this mechanism.[8] We believe that there is a coexistence of the two mechanisms (tip-growth mechanism and base-growth mechanism) in the CVD growth of lattice-orientated carbon nanotubes. Therefore, though there is no movement of catalysts based on base-growth mechanism, interaction between catalyst and substrate still affects the result because stronger interaction limits catalysts' ability to move around the substrate and leads to a higher percentage of carbon nanotubes formed based on the base-growth mechanism, which is shorter compared to carbon nanotubes formed based on the tip-growth mechanism,[8,10] and thus results in SWNTs with a lower average length. On the basis of the discussion above, we can see that interaction between catalysts and substrate essentially increases the activation energy of the reaction and decreases the rate of SWNTs formation. The strong Fe−quartz interaction also hampers the catalysts from lifting up from the substrate and decreases the density of gas flow-directed carbon nanotubes. According to the explanation made above, we can safely draw the conclusion that weaker interaction between catalysts and substrate leads to longer lattice-orientated carbon nanotubes and denser gas flow-directed carbon nanotubes. Therefore, we can get better cross-bar-structured carbon nanotubes when the interaction between catalysts and substrate is weaker.

In summary, based on the two mechanisms for SWNT's growth, we developed an approach to grow SWNTs cross-bar on ST-cut quartz surface in one batch. The approach combines the advantage of gas flow-directed growth mode at growing large area SWNT arrays and the advantage of lattice-orientated growth mode at growing high density SWNTs array; thus we can get large area SWNTs cross-bar with high node density by applying this method and the result is better compared to processes reported before. To grow large area well-aligned SWNTs cross-bar, it is crucial to find the optimal growing condition for such structure. Growing temperature and interactions between catalyst and substrate are identified as critical factors for fabrication of SWNTs cross-bar. The SWNTs cross-bar will find wide applications for future nanodevices.

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