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Lattice-directed growth of single-walled carbon nanotubes with controlled geometries on surface

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ABSTRACT

How to control the orientations of single-walled carbon nanotubes (SWCNTs) on surface is the key point to controlling their geometries. In this work, we chose quartz (001), MgO (001) and layered mica with 3-, 4- and 6-fold symmetry, respectively as substrates to grow SWCNTs using gas-flow and lattice-directed modes. The produced SWCNTs were aligned along the symmetrical directions and displayed the homologous angles of 120°, 90° and 60° during growth on quartz (001), MgO (001) and mica surfaces, respectively. The obtained SWCNTs with controlled geometries would have wide applications in nanoelectronic devices in the future.

Single-walled carbon nanotubes (SWCNTs) have been regarded as one of the promising candidates for future applications in nanoelectronic devices [1]. However, how to control the geometry of SWCNTs on surface is a great bottleneck to the fabrication of nanoelectronic devices. Till now, the gas-flow and lattice-directed modes have been used to grow aligned SWCNTs on surface [2,3]. Following these two modes, ultra-long, serpentine and cross-bar SWCNTs on Si, sapphire or ST-cut quartz substrates have been produced [2,4–6]. Generally speaking, the gas-flow-directed mode follows the "kite-mechanism" with the catalyst nanoparticles floating in the gas flow at a high growth temperature (>900 °C) [3], while the lattice-directed mode bases on the energy differences with the SWCNTs selectively directed along some preferential orientations on single crystal substrates. Therefore, both the growth temperature and used substrates play an essential role to the geometry control of SWCNTs [2,7]. As we know, all kinds of single crystals present only 5 different symmetries of 1- (0°), 2- (180°), 3- (120°), 4- (90°) and 6- (60°) fold. If the growth substrate surfaces present multiple symmetries, the obtained SWCNTs along different directions on surface should possibly show complex geometries. Herein, quartz (001), MgO (001), and layered mica were used as the substrates to grow SWCNTs, which have the 3-, 4- and 6-fold symmetries, respectively as shown in Fig. 1. Using the gas-flow-directed mode or lattice-directed mode, it is expected that the produced SWCNTs can be oriented along the different symmetrical directions and display the preferential angles of 120° on quartz, 90° on MgO and 60° on mica.

All the crystal substrates used in our experiments with no miscut angles must previously undergo a necessary annealing process for a better crystallization (quartz and mica at 900 °C for 8 h, MgO at 1000 °C for 12 h). The iron as catalyst and ethanol as carbon source were used to grow SWCNTs for 30 min in atmospheric pressure chemical vapor deposition. Under the lattice-directed mode, a mixture of 180 sccm H_2 and ethanol vapor by bubbling 80 sccm Ar were introduced, and the SWCNTs were produced at 850 °C from a spin-coated iron catalyst (3000 rpm for 1 min). Under the gas-flow-directed mode, a mixture of 300 sccm H_2 and ethanol vapor by bubbling 100 sccm Ar were introduced, and the SWCNTs were pro-

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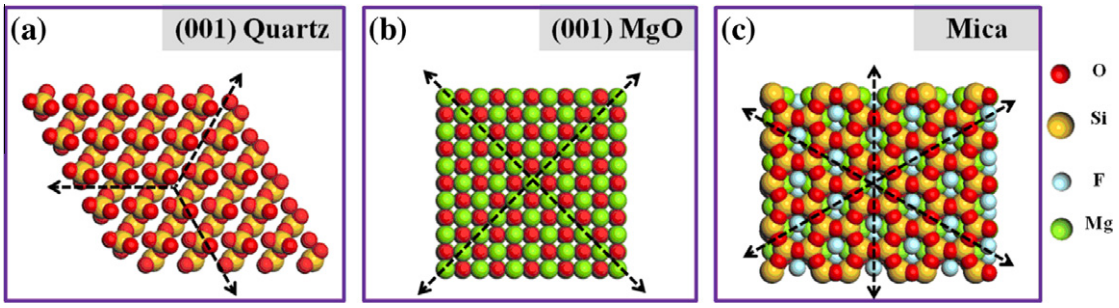

Fig. 1 – (a)–(c) Atomic diagrams of quartz (001), MgO (001) and layered mica surfaces with 3-, 4- and 6-fold symmetry, respectively. The black arrows show the possible growth directions of SWCNTs. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

duced at 950 °C from the patterned iron catalysts prepared by a micro-contact printing method [4].

During the SWCNT growth process, there are two main forces of lattice-alignment force (F_r) and shear friction force (F_u), which compete to determine the geometry of the SWCNTs [8]. Following the lattice-directed mode, the SWCNTs were produced on quartz, MgO and mica surface at 850 °C as shown the scanning electron microscope (SEM) images in Fig. 2(a)–(c). Due to the weak F_u, the SWCNTs should always keep their growth on the substrate and further be oriented along particular crystallographic directions by the strong F_r. As shown in Fig. 1(a), the quartz (001) surface with threefold symmetry shows 3 identical directions (the yellow arrows). Therefore, the grown SWCNTs were oriented along these directions because of the strong adsorption energies with the substrate (Fig. 2(a)). The aligned SWCNTs also presented a directional transformation with leaving a special angle of 120° due to the possible thermal perturbation or crystal defect. Moreover, when the growth tip met the SWCNT itself, the growth could be self-terminated and form the geometry of a closed polygon. Similarly, the MgO (001) and layered mica surfaces possess 4 and 6 identical directions to preferentially align the SWCNTs during their growth (Fig. 1(b) and (c)). The SWCNTs produced on MgO surface with the crossed geometry displayed the special angles of 90°, while the SWCNTs on mica surface had the angles of 60° and 120° as shown in Fig. 2(b) and (c). It was also found that the frequency of 120° were more than that of 60°.

Following the gas-flow-directed mode, the SWCNTs with controlled geometries were produced at 950 °C as shown in Fig. 2(d) and (f). In this way, both the F_u and F_r should simultaneously align the produced SWCNTs along their own force directions. At 950 °C, the F_u by convection flow was strong enough to lift the catalyst and SWCNTs, which kept on a floating state in the gas flow during growth [3]. When the growth process ended, the SWCNTs would fall off due to the decreased F_u. Once they began to touch the substrate surface, the F_r could drive the SWCNTs to change their directions along the preferential directions. As the SEM image in Fig. 2(d), the grown SWCNTs with a serpentine geometry had a directional transformation of 120° on the 3-fold symmetrical quartz surface. On the MgO and mica surface, there were

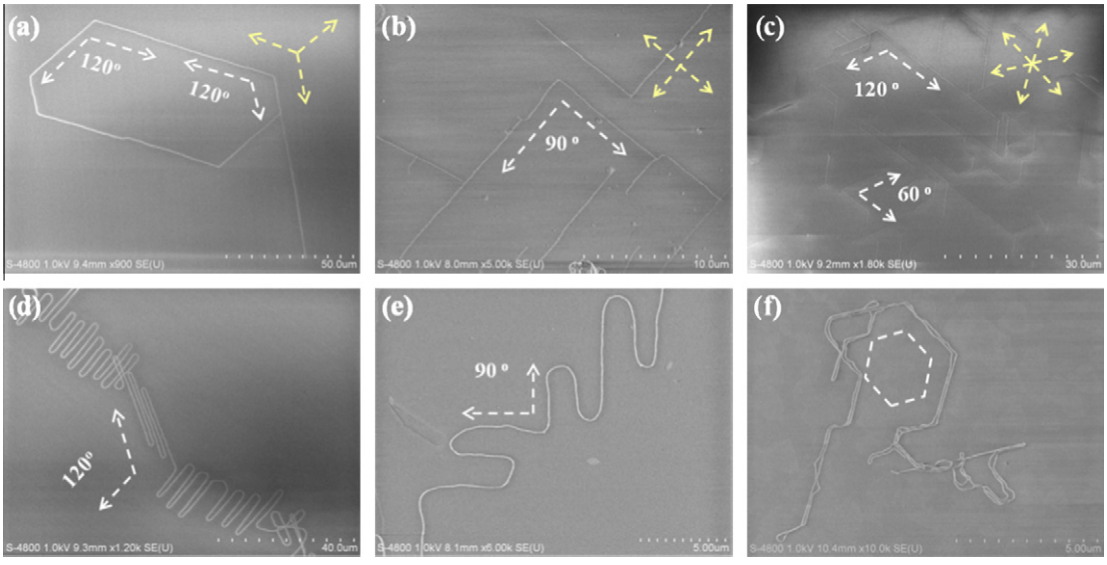

Fig. 2 – SEM images of grown SWCNTs at 850 °C (a)–(c) and 950 °C (d)–(f) with 120° on quartz, 90° on MgO and 60° (120°) on mica, respectively. The yellow arrows show the expected growth directions of SWCNTs. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

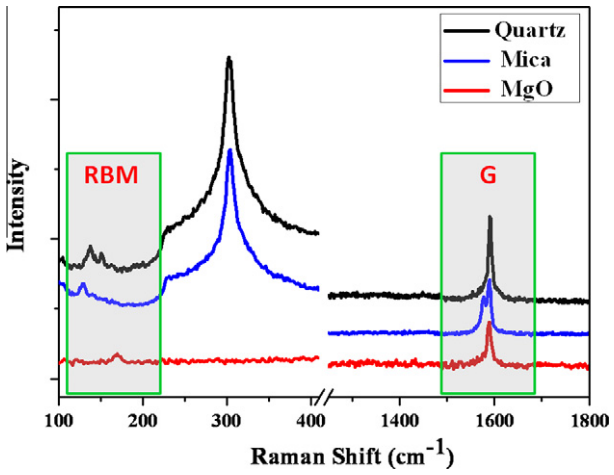

Fig. 3 – Raman spectra of SWCNTs with RBM and G bands. The SWCNTs grown on quartz and mica surfaces were transferred onto SiO_2/Si substrates.

the different lattice-alignment forces along 4 and 6 identical directions, and thus the obtained serpentine SWCNTs displayed the step-like and hexagon geometries with 90° and 120° (Fig. 2(b) and (c)). Furthermore, the SWCNTs grown on quartz and mica surfaces were transferred onto SiO_2/Si substrates. As shown in Fig. 3, the typical Raman spectra with radial breathing mode (RBM) and G bands showed that the grown carbon nanotubes were single-walled. In this way, the geometry of SWCNTs can be rationally controlled by adjusting the temperature and substrate with different symmetries.

As to the mechanism of lattice-directed mode, the "valleys" existing on sapphire surfaces were proposed to play an essential role to orientate the SWCNTs [9,10]. Although we have not observed these "valleys" on our used substrates, it was confirmed that the SWCNTs with the angles of 120° on quartz, 90° on MgO and 60° on mica were aligned along the surface lattice-directions. Using this rational approach, the obtained SWCNTs with controlled geometries would have potential applications in nanoelectronic devices.

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