Focused ion beam milling as a universal template technique for patterned growth of carbon nanotubes

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Focused ion beam (FIB) milling system has been used to create nanosized patterns as the template for patterned growth of carbon nanotubes on Si substrate surface without predeposition of metal catalysts. Carbon nanotubes only nucleate and grow on the template under controlled pyrolysis of iron phthalocyanine at 1000 °C. The size, growth direction, and density of the patterned nanotubes can be controlled under different growth conditions and template sizes. Atomic force microscopy and electron microscopy analyses reveal that the selective growth on the FIB template is due to its special surface morphology and crystalline structure. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2710785]

Patterned growth of carbon nanotubes (CNTs) has been reported on silica (SiO_2) substrates using various chemical vapor deposition (CVD) methods.[1] Relatively, it is difficult to grow CNTs on pure Si surface using the same approach without a predeposition of metal catalysts. Recently, it is found that patterned growth on the Si wafer surface can be achieved by mechanically scratching the smooth Si wafer before the CVD process,[2] which suggests that nanosized surface structures could serve as the template for helping nanotube patterned growth. We report in this letter that focused ion beam (FIB) milling technique can be used to create such nanosized template on Si substrates and selective growth of CNTs can be achieved under controlled growth conditions. FIB has been used to help catalyst deposition for CNT selective growth,[3] but it has not been used as a templating technique previously. FIB is becoming an important tool to create different structures at nanoscale on different surfaces;[4] the FIB template technique will have many applications in nanodevice design and construction.

Patterned templates were created using a dual focused ion beam system (Orsay Physics-Jeol Camion 6460LVSEM) with Ga ions at ion beam energy of 30 keV and a current of 1.5 μA on polished Si (100) wafer surface and parallel trenches can be seen from the scanning electron microscopy (SEM) image in Fig. 1(a). The trench width can be varied from several nanometers to several hundreds nanometers by adjusting the beam size. The trench depth is normally in the range from 10 to 100 nm depending on the scan speed. The typical trench structure can be seen from the image of an atomic force microscope (AFM, a nanoscope III Multimode) in Fig. 1(b). Trenches with different sizes and shapes were created to serve as templates for nanotube selective growth.

Iron phthalocyanine (FePc) was used as the precursor material because carbon nanotubes have been produced previously via a controlled pyrolysis process.[5,6] A ceramic combustion boat containing 0.1 g of FePc powder was placed inside a quartz tube about 7 cm away from the furnace center. The patterned Si wafer was inserted at the middle of a tube furnace to collect the deposition and CNTs. An Ar–5% H_2 gas flow (about 75 cm^3/min) was used as material carrier gas to transfer C vapor to the substrate. When the furnace temperature was set at 1000 °C, the temperature profile of the furnace indicates that the substrate temperature should be the same as the furnace temperature and the boat containing FePc at the temperature zone around 800 °C. This temperature is higher than the vaporization temperature of FePc (600 °C).[6,7] FePc vapor was generated and transferred by Ar gas flow into high temperature zones where pyrolysis occurred and CNTs were formed.[8] Some nanotubes will deposit on the patterned Si substrates.

The SEM image in Fig. 1(c) shows a FIB created pattern with parallel trenches coated by CNTs after heating at 1000 °C for 3 min. The CNTs have a diameter ranging from 20 to 50 nm and grow out along the substrate surface up to 20 μm because the substrate was placed *horizontally* in a horizontal tube furnace. The growth direction is parallel to the carrier gas flow. The CNTs nucleate only inside the FIB trenches and no CNTs are found to nucleate on the surrounding flat surface. Transmission electron microscopy reveals a typical multiwalled cylindrical structure of these nanotubes. Using the same heating temperature, gas flow rate, and substrate location, the selective growth of standing CNTs in a higher density was achieved on a patterned substrate of two crossed trenches when the substrate was placed *vertically* to face the coming gas flow during the heating. In this case, more C vapor was stopped by the substrate and thus a large number of large clusters of CNTs, instead of individual nanotubes, are formed along the trenches [Fig. 1(d)]. Each cluster contains a large number of standing CNTs. Because of the large partial vapor pressure, a few clusters were even formed on the flat surface of Si substrate, but preferred nucleation of CNT clusters along the trenches can be seen clearly. The formation of the large CNT clusters suggests that the vapor deposition over the trenches might take place first and then the CNTs grow out from the deposition.

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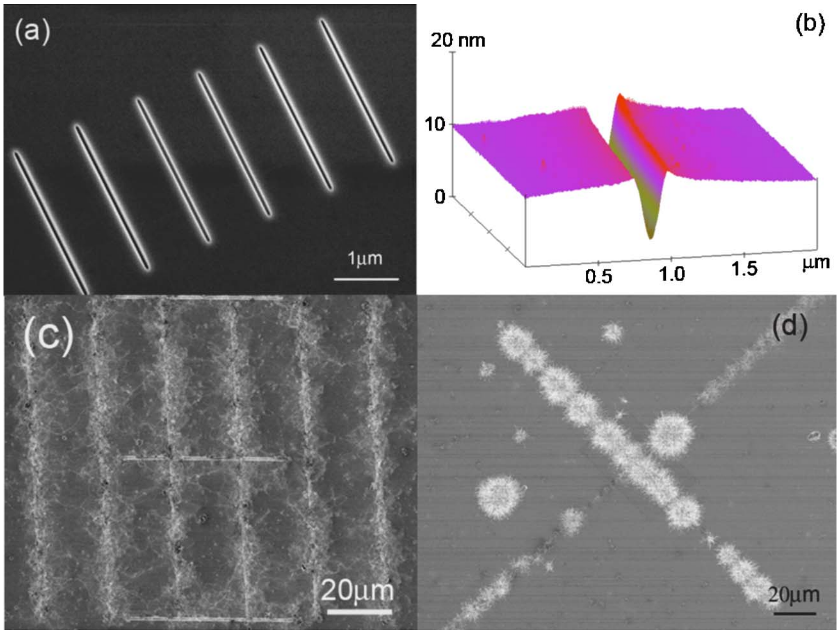

FIG. 1. (Color online) (a) SEM image of parallel trenches created by FIB without CNT coating, (b) typical AFM scan image of a FIB trench, (c) SEM image of selective growth of CNTs in the patterns created using FIB, and (d) SEM image showing the formation of CNT clusters along the trenches under a high-pressure vapor condition.

The nanotube density and length can be controlled further by adjusting growth conditions and trench size. A Si substrate with wide trenches (about 1 μm wide) was placed *horizontally* 10 cm away from the combustion boat. The longer distance between the source materials and the patterned substrate produces a lower partial vapor pressure over the substrate and a lower substrate temperature of around 850 °C. Under such conditions, fewer and shorter nanotubes will be formed on the substrate so that the nucleation process on a wide trench can be seen clearly.[9] After heating at 1000 °C, many small particles are formed only on the two crossed trenches as shown in Fig. 2(a), indicating a selective vapor deposition on the wide trenches. More interestingly, Fig. 2(b) shows single nanotube growing out from some particles. A nanotube of about 50 nm in diameter attached on a large particle (200 nm in diameter) sits at the boundary area between the trench and the flat substrate surface [Fig. 2(c)]. Elemental analysis using x-ray energy-dispersive spectroscopy has found both C and Fe elements, suggesting the particles as decomposed FePc. The particles attached with a nanotube further confirm that the C(Fe) vapor first deposits inside the trenches and then CNTs grow out from the deposition.[10]

The growth mechanisms of the above patterned CNTs on FIB templates are illustrated in Fig. 3. For the narrow and deep FIB trenches with the width close to the nanotube diameter, capillarity effect is responsible to the preferred vapor deposition inside the trenches.[2,11] Therefore, nanotubes root inside the trenches [Figs. 3(a) and 3(b)]. The growth direction (horizontal or vertical alignment) can be controlled by varying the carrying gas flow direction related to the substrate surface. Chen and Yu have reported previously the growth direction control of nanotube layers by changing carrier gas flow directions.[7] When the vapor pressure is higher, larger deposition will be produced over the trenches and nanotube clusters are therefore formed [Fig. 1(d)].

For wide trenches, the capillarity effect is less important. The preferred deposition could be considered from the following effects: (1) In surface morphology effect, the growth probability of a new crystal on a flat surface is proportional to the binding energy E of the deposited atom,[12] where

$$E = \alpha \frac{q^2}{a}.$$

q is the charge of ion, a is the lattice constant, and α is a numeric factor depending on the site of deposition.

Because $\alpha(\text{corner}) > \alpha(\text{edge}) > \alpha(\text{faces})$, the deposition prefers the edges and atomic corners on a flat surface in the case of low saturated vapor pressure. The FIB trenches provide a large number of atomic corners and edges as revealed by AFM measurement. The AFM scan profile of a FIB trench in Fig. 3(c) shows that high shoulders are the build up of Si debris and Ga ions.[4] The trench surface is not smooth and a highest roughness was measured at 0.33 nm, which is double

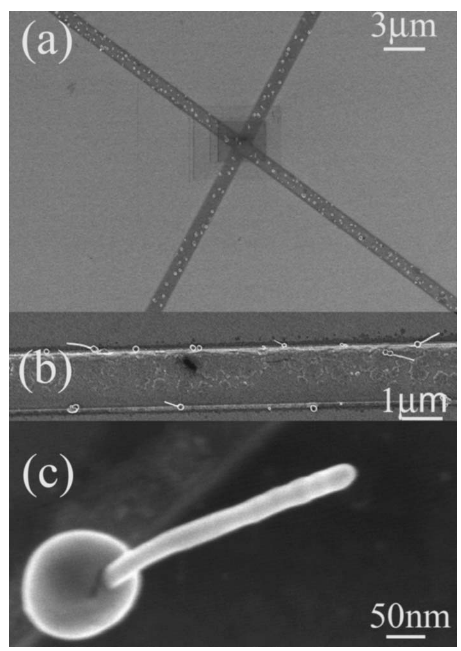

FIG. 2. (a) SEM image showing selective deposition on two crossed FIB trenches under a low vapor density and at a lower temperature, (b) SEM image revealing nanotube growth from many nanoparticles deposited on a FIB trench, and (c) SEM image showing a nanotube growing out from a large deposition particle sitting at the edge of the trench.

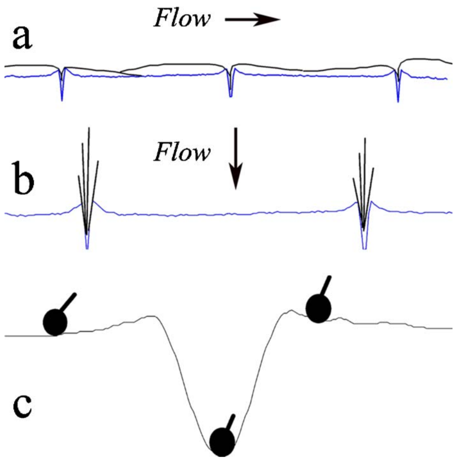

FIG. 3. (Color online) (a) CNTs root inside narrow trenches and grow along the substrate surface when the substrate is parallel to the vapor flow direction, (b) High-density and vertically standing CNTs growing out from narrow trenches when the substrate is facing to the C vapor flow, and (c) AFM profile of a FIB trench revealing possible nanotube nucleation sites under low vapor pressure condition.

the roughness of the polished flat Si surface (0.16 nm). Compared with the SEM images of Figs. 2(b) and 2(c), possible nucleation sites are marked in Fig. 3(c). (2) In surface structure effect, Fig. 2(a) suggests that the special structure of the trenches should also affect the vapor deposition compared with the flat crystalline Si substrate.[13] The regions of the Si substrate exposed under the focused Ga ion beam are amorphized to a thin layer.[14] Beneath the amorphous layer, the region is heavily damaged with a high point defect concentration. In addition, Ga ions are implanted into the surface and exist in the near surface. Although most Ga vaporized during the subsequent annealing and amorphous surface will recrystallize when the temperature is up to 1000 °C, the disordered surface structure helps the selective deposition.[15] The vapor prefers to deposit on an amorphous surface than a perfect smooth crystalline surface because of a smaller lattice mismatch and thus less stress generates at the interfaces. The lattice constant in the above equation of amorphous phase is smaller than that of crystalline phase. Therefore, more energy is liberated when a new atom deposits on amorphous substrate surface.

In summary, patterned growth of CNTs has been achieved on the template created by FIB on smooth Si substrates without predeposition of metal catalysts. SEM and AFM analyses reveal that the FIB patterns are the preferred deposition sites for the C vapor due to surface roughness, capillarity effects, and a disordered structure. The patterned CNTs with different orientations, densities, and sizes can be produced. Because selective nucleation inside FIB trenches does not depend on the materials of the substrate, this FIB template technique could be applied for selective growth of other nanotubes and nanowires on any flat substrates.

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