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Mechanism of Selective Growth of Carbon Nanotubes on SiO₂/Si Patterns

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ABSTRACT

During the chemical vapor deposition of multiwalled carbon nanotubes using the vapor phase delivery of a metal-organic (ferrocene) catalyst precursor, a strong selectivity for growth on patterned SiO₂/Si substrates has been observed. A mechanism for this selective growth is described here. Delivered metal particles (Fe) on Si and SiO₂ regions were investigated using several high-resolution characterization techniques. Active iron catalyst (γ iron) particles were formed on the silicon oxide surface resulting in the formation of highly aligned nanotubes on this substrate. However, in the Si regions, stable FeSi₂ and Fe₂SiO₄ particles were formed due to chemical reactions between silicon surface and Fe particles at high temperature leading to an inhibition of nanotube growth in the Si regions.

Carbon nanotubes have attracted considerable interest due to their unique one-dimensional structure and superior electrical and mechanical properties.^{1–4} Particularly, carbon nanotubes have fascinating electrical properties such as high current density (10⁹ Amps/cm²)⁵ and ballistic conductance⁶ by virtue of their one-dimensional electronic structure. These features have led to their potential use as nanotube interconnects in microelectronic devices. To build an integrated nanotube-based system, it is essential to fabricate carbon nanotubes on designed substrates in a controllable manner. Our previous publications have reported a method for highly organized carbon nanotube growth selectively on the patterned SiO₂/Si substrates using a vapor phase ferrocene/xylene delivery method, i.e., nanotubes grow only on the SiO₂ surfaces and leave the Si substrates blank.^{7–9} The level of control provided by this method enables us to construct complex carbon nanotube architectures, which can fulfill their potential applications such as active elements in field emission displays, sensors, and electronic devices. However, there has been no clear explanation for the mechanism of this site selectivity. Here we report the studies that clearly elucidate the mechanism of nanotube growth selectivity on SiO₂ vs Si.

Multiwalled carbon nanotubes were produced using a thermal chemical vapor deposition (CVD) method by exposing a mixture of ferrocene and xylene vapor to the patterned SiO₂/Si substrates at 800 °C for 10 to 20 min.^{7–11} For the substrate preparation, a SiO₂ layer (of a thickness of 100

nm or greater, grown by plasma enhanced CVD (PECVD) or thermal oxidation method on pristine Si (001) wafer), was prepared and patterned by conventional photolithography. Then etching of silicon oxide was performed using hydrofluoric acid solution. The prepared substrates were subsequently cleaned ultrasonically in acetone and deionized water and placed into a tube furnace. Pressure was maintained around 100 mTorr and an argon gas atmosphere was supplied to prevent the patterned SiO₂/Si substrate surface from oxidation. After the furnace was heated to the deposition temperature of 800 °C, a solution of ferrocene (0.4 mg) in xylene (10 mL) was prevaporized at 150 °C and introduced into the quartz tube. Due to the pressure difference between the cylinder consisting of the prevaporized ferrocene–xylene mixture and the CVD system, the catalyst and carbon sources are automatically introduced into the furnace chamber to grow carbon nanotubes. Xylene acts as the source of carbon atoms, while Fe from ferrocene serves as the catalyst for multiwalled carbon nanotube growth. Aligned carbon nanotubes were grown selectively on the patterned SiO₂ structures but not on the silicon surface.

Scanning electron microscopes (JEOL 6330F FESEM and Hitachi S-5000 HRSEM) were employed to characterize the growth of carbon nanotubes and surface morphology of the designed substrates after nanotube growth. To examine morphology of the SiO₂ surface area, the grown nanotube layer was partially removed using tweezers. For the elemental analysis over the substrates after carbon nanotube growth, an electron probe microanalyzer (EPMA) with wavelength-

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dispersive spectroscopy for X-rays (JEOL: JXA-8621 WDS) and an Auger electron spectroscopy (AES: PHI 670) were used. A transmission electron microscope (TEM: Hitachi H-9000) operated at 300 keV was employed to characterize the structure of catalyst particles and carbon nanotubes on the substrate. For obtaining the diffraction patterns of particles formed in silicon and silicon oxide matrix, an electron beam with 20–30 nm diameter was used to minimize contributions from SiO₂ and Si, which otherwise might affect the interpretation of the results. For the TEM sample preparation for cross sectional observation, carbon and tungsten films were deposited on the surface of the interested areas to protect the interested surface from ion damage. Then, extra materials were removed from both sides of the interested region using a focus ion beam (FIB: Hitachi FB-2000A), until a very thin (electron microscopy transparent) specimen (250 nm) was obtained. The thinned part was then removed from the substrate and mounted on a copper mesh using a “microsampling technique”.¹²

Figure 1a is a typical SEM image of the selective growth of aligned multiwalled carbon nanotubes on patterned SiO₂/Si structures. It is clearly seen that carbon nanotubes have grown vertically only on the patterned SiO₂ structures (about 100 nm in thickness) and form aligned nanotube arrays on the designed structures inheriting their original shapes and size precisely (10 μ m in width), while leaving the Si areas blank. The height of these nanotube pillars is about 50 μ m and can be controlled by changing the time of CVD process. The vapor phase catalyst delivery method mentioned here is different from that used in conventional thermal CVD methods in which patterned catalysts on the designed positions need to be deposited on the substrate surfaces before CVD.^{13–16} Therefore, in this method, vapor phase catalyst, Fe, and carbon source are supplied at the same time all over the substrate at high temperature (800 °C), making the process relatively simple in comparison to other methods. Figure 1b,c shows the surface morphology of Si and SiO₂ areas. A close view of the surface shows that many particles are formed on the silicon surface, but these apparently do not aid in carbon nanotube growth (Figure 1b). A dense film of particles is also observed on the silicon oxide surface where aligned nanotubes grow very well (dense aligned nanotubes were removed in Figure 1c). Particle sizes are observed to be around 20–40 nm in the silicon oxide region but larger in the Si region. EPMA and AES data indicated that iron and carbon are dispersed over both the silicon and the silicon oxide region during CVD. Only carbon was detected on the as-grown surface on the Si area by AES. However, after sputtering in situ with 3 keV argon ions for 30 min, iron and silicon signals could be detected, indicating the presence of a thin carbon over layer on the Si area.

Clear information on these Fe-containing particles after nanotube growth could be obtained by cross-sectional TEM observation of the substrates. TEM images of the cross section of the substrates after CVD growth of nanotubes are shown in Figure 2. On the SiO₂ area, nanotubes as well as Fe-containing particles can be easily identified even after removing most of the aligned nanotubes (Figure 2a,c).

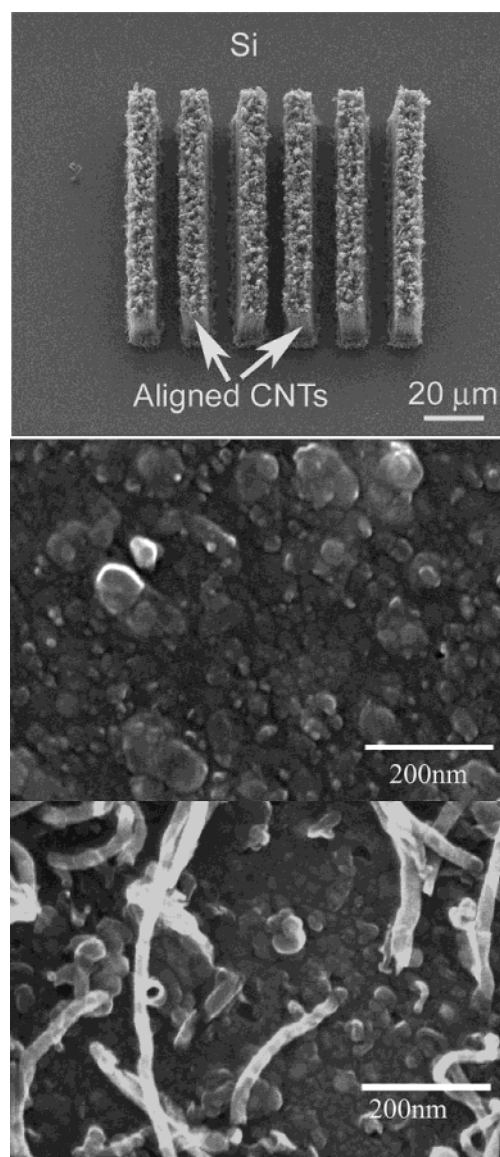


Figure 1. SEM images of selective growth of carbon nanotubes on patterned SiO₂/Si substrate using the vapor phase ferrocene/xylene delivery method. (a) Selective growth of aligned multiwalled carbon nanotubes on the patterned SiO₂/Si substrate. (b) Close observation on the bare silicon surface where no nanotubes have grown. (c) Surface morphology of silicon oxide region after scratching carbon nanotubes, a few nanotubes remained on the silicon oxide surface.

Irregularly shaped particles of 10 to 40 nm in diameter appear on the top surface of the oxide area as well as inside the cavities of nanotubes. Nanotubes having 30–40 nm diameters are grown from these dispersed particles. While on the surface of Si area no trace of nanotubes is found, but larger precipitates of submicron size particles are observed beneath the surface (Figure 2b,d).

Selective area electron beam diffraction results shown in Figure 3 indicate that the formed irregular-shaped nanosize particles on the top of silicon oxide surfaces are pure gamma iron (fcc Fe), which is an active catalyst for carbon nanotube growth on the SiO₂ region. However, on the silicon surface, diffraction patterns suggest the formation of iron silicide and iron silicate. A cross-sectional image of the silicon region

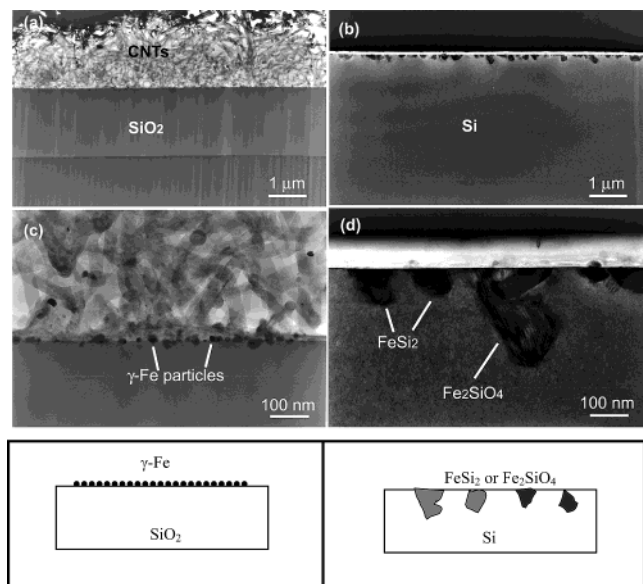


Figure 2. TEM images of the cross section of the substrates. (a) SiO₂ area after CVD growth and removing of carbon nanotubes. (b) Si area without any nanotube growth but precipitate of submicron-size particles near the surface. (c) Enlarged picture from the nanotube/SiO₂ interface in (a) showing the formation of gamma iron particles on silicon oxide surface and the growth of nanotubes from the particles formed. (d) Enlarged area from (b) showing the formation of iron silicide and iron silicate crystals during CVD processing. Corresponding schematics are also illustrated.

shows that during the CVD processing, nucleation of these new phases occurs from the silicon surface and grow into the Si matrix (particle size about 50–100 nm), Figure 2d. Compared with gamma Fe particles having irregular shapes on the silicon oxide surface, these crystallized particles inside the silicon matrix were formed with well-defined shapes showing stable compound formation through chemical reaction between Si and vapor phase Fe during high temperature CVD process. Electron beam diffraction results on these crystallized particles indicated that the particles are mainly iron silicide (FeSi₂, Figure 3b) and iron silicate (Fe₂SiO₄, Figure 3c).

From the above results, we draw the conclusion that on the silicon oxide region, the high activity of carbon in the gas phase drives carbon to dissolve into Fe particles formed on the substrate surface during decomposition of ferrocene at high temperature. The Fe particles may thus easily become saturated or supersaturated with carbon atoms, and the precipitation of carbon from the surface of the Fe particle leads to the formation of tubular carbon solids in sp² structure. Iron particle is chemically stable on the silicon oxide during the full CVD process time. Therefore, the gamma Fe catalysts with small dimensions can effectively catalyze the growth of highly dense carbon nanotubes on the SiO₂ region. However, on the silicon surface, a chemical reaction occurs between the silicon, Fe, and oxygen, which exists in small concentrations in our vacuum system.¹⁷ This reaction is dominated by diffusion of Fe through the native silicon oxide layer at high temperature.¹⁸ These results in a complete change of the chemical nature of the deposited Fe particles from an active Fe catalyst to stable compounds such

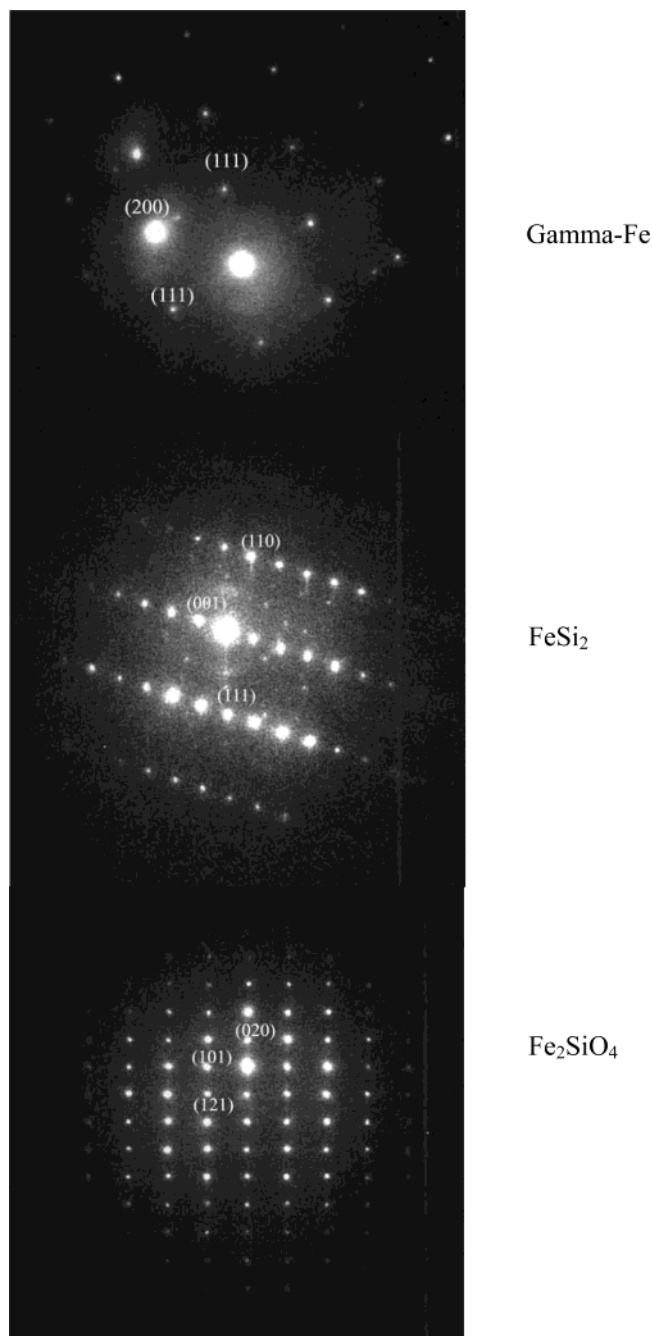


Figure 3. Selective area diffraction patterns from the particles on the oxide surface (Figure 2c) and on the Si surface (Figure 2d), indicating gamma iron (fcc Fe) formation and iron silicide and iron silicate formation during the CVD process on silicon oxide surface and silicon surface, respectively.

as iron silicide (FeSi₂) and iron silicate (Fe₂SiO₄), which are known for their noncatalytic activity for carbon nanotube growth.¹⁹

In conclusion, the selectivity of multiwalled carbon nanotube growth on SiO₂ and Si was studied using the vapor phase catalyst delivery method on patterned SiO₂/Si substrates. Active gamma iron (γ-Fe) catalysts that effectively prompt the growth of carbon nanotubes are formed on the SiO₂ surface. The formation of iron silicide (FeSi₂)/iron silicate (Fe₂SiO₄) particles on the silicon surface during the high temperature deposition process creates catalytically

inactive Fe compounds, and hence no nanotube growth is found. We believe that the chemistry of catalyst particles on substrate is very important for growing carbon nanotubes. These results will enable us to select more suitable substrates for further designing of carbon nanotube architectures.

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