

Silicon oxide thickness-dependent growth of carbon nanotubes

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Recent discovery of substrate-selective growth of carbon nanotubes on SiO₂ in exclusion to Si, has opened up the possibility of organizing nanotubes on Si/SiO₂ patterns in premeditated configurations for building devices. Here, we report the strong dependence of nanotube growth on the SiO₂ layer thickness, and the utility of this feature to build three-dimensional architectures. Our results show that there is no detectable nanotube growth on SiO₂ layers with thickness (T_{SiO_2}) less than ~ 5 –6 nm. For $6 \text{ nm} < T_{\text{SiO}_2} < 24 \text{ nm}$, the nanotube growth rate increases monotonically with increasing oxide thickness, and then saturates as T_{SiO_2} approaches $> 50 \text{ nm}$. We grew nanotubes with multiple lengths at close proximity in a single step by using substrates with regions of different T_{SiO_2} . Such processing strategies would be attractive for creating nanotube mesoscale architectures for device applications. © 2004 American Institute of Physics. [DOI: 10.1063/1.1636826]

Carbon nanotubes (CNTs) are fascinating molecular structures with attractive electronic, thermal, and mechanical properties. There is a great deal of interest in growing aligned CNTs since they allow the possibility of harnessing the collective anisotropic properties of individual nanotubes, and make CNTs amenable for applications such as in field emission,¹ sensing,^{2,3} actuation,^{4,5} and switching.⁶ While vertical growth of aligned CNTs on large areas ($\sim \text{cm}^2$) by chemical vapor deposition (CVD) has been extensively reported,^{1,7–10} progress remains slow in producing multilayered CNT structures with controlled tube orientations (other than vertical) and coupling them with tunable tube lengths.

Recently we demonstrated a substrate-selective CVD process using xylene and ferrocene to selectively grow CNTs on SiO₂—in exclusion to Si surfaces—in an orientation parallel to the SiO₂ surface normal.¹¹ By carrying out this process on lithographically chiseled silica patterns of different shapes on silicon substrates, one can grow three-dimensional (3D) architectures with CNTs of preselected orientations at premeditated locations.^{12,13} Strategies such as altering the substrate surface chemistry, e.g., by depositing other materials on the SiO₂ surfaces, have also been used to obtain 3D CNT architectures. For example, patterns of a noncatalytic material (e.g., Au^{14,15} or Ag¹⁶) can be used to selectively inhibit or prevent CNT growth, and provide control over the CNT length in regions of the substrate where the catalyst is at least partially active.¹⁵ A sputtered Al film was reported to enhance CNT growth, and produced longer tubes than the nanotubes grown in the bare quartz area.¹⁷

In this letter, we show that the CNT growth rate can be adjusted by merely altering the SiO₂ layer thickness. We demonstrate that this dependence can be utilized to devise a simple and powerful alternate strategy for tuning CNT length

and building 3D architectures in instances where altering the surface chemistry by extraneous means may not be feasible.

The substrates used in our experiments were Si(001) wafers capped with thermally grown SiO₂ layers of thickness ranging from 3.5 nm up to 1 μm . The SiO₂ layers were grown in a Tystar Mini Tytan 3-stack furnace by dry oxidation at 700–850 °C for 60–175 min. The SiO₂ thickness (T_{SiO_2}) was determined by variable angle spectroscopic ellipsometry at angles between 60° and 70°. CVD was carried out at 800 °C on these SiO₂ substrates using a ferrocene/xylenes (0.4 g/40 ml) mixture as the feeding source, as described previously.^{8,14,15} In our experiments, the CVD time interval (t_{CVD}) for nanotube growth was varied from 3 to 30 min. In order to average out the influence of carbon source fluctuation inside the furnace on the CNT growth, we used $0.5 \times 0.5 \text{ cm}^2$ SiO₂ pieces and placed them randomly in the furnace but close to each other. The CNT length (L_{CNT}) was determined by measuring sample cross sections by scanning electron microscopy (SEM) in a JEOL JSM-6330F instrument equipped with a field-emission electron gun. Figure 1 illustrates the salient features of the experimental procedure.

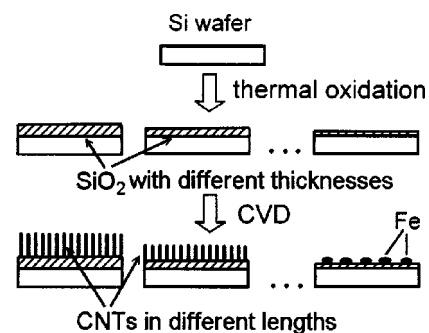


FIG. 1. Schematic sketch illustrating the preparation of substrates with various SiO₂ thicknesses (T_{SiO_2}), and subsequent CVD growth of CNTs with different lengths (L_{CNT}).

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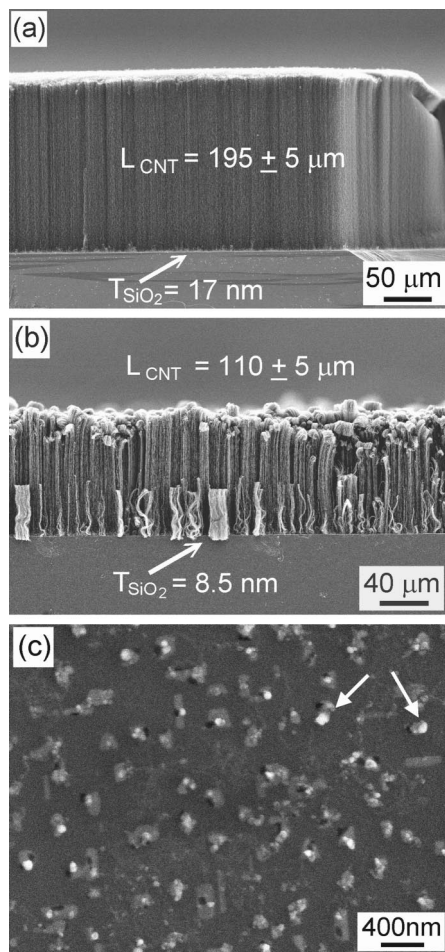


FIG. 2. SEM images of as-grown aligned CNTs on SiO₂ samples for a CVD reaction time of 30 min. (a) $L_{\text{CNT}} \sim 195 \mu\text{m}$ on $T_{\text{SiO}_2} = 17 \text{ nm}$, (b) $L_{\text{CNT}} = 110 \mu\text{m}$ on $T_{\text{SiO}_2} = 8.5 \text{ nm}$, and (c) Fe-C particles on $T_{\text{SiO}_2} = 3.5 \text{ nm}$ (see arrows).

Changing the SiO₂ layer thickness (T_{SiO_2}) results in the alteration of the CNT film thickness, i.e., the CNT length (L_{CNT}). For example, 30 min CVD on a 17-nm-thick SiO₂ layer produces an average CNT length of $\sim 195 \mu\text{m}$, while for $T_{\text{SiO}_2} = 8.5 \text{ nm}$, L_{CNT} is much shorter at $\sim 110 \mu\text{m}$ [see cross-section SEM images in Figs. 2(a) and 2(b)]. There is no observable CNT growth on $T_{\text{SiO}_2} < 5 \text{ nm}$, instead, we see regions of white contrast from $\sim 50 \text{ nm}$ particles [see arrows in planar-view Fig. 2(c)], which have been identified to contain γ -Fe and carbon.¹⁸

Figure 3 summarizes the thickness dependence of CNT growth on the SiO₂ layer ranging from ~ 3.5 to 24 nm, for three different CVD time intervals. For each time interval, L_{CNT} increases rapidly with T_{SiO_2} , up to $T_{\text{SiO}_2} \sim 20 \text{ nm}$. For example, for 30 min CVD, L_{CNT} increases by $\sim 11 \mu\text{m}$ for every 1 nm increment T_{SiO_2} . We note that L_{CNT} decreases dramatically and approaches zero for $T_{\text{SiO}_2} < \sim 5 \text{ nm}$, irrespective of the CVD time. This indicates that T_{SiO_2} should be greater than a threshold value of ~ 5 – 6 nm to obtain CNTs by our CVD process. Above this value, the CNT length can be tuned by adjusting the SiO₂ layer thickness.

Examination of L_{CNT} vs t_{CVD} plots for different SiO₂ thicknesses [Fig. 4(a)] shows that the CNT growth rate is a constant for a given SiO₂ thickness, and increases monotonically with T_{SiO_2} . Inset in (b) shows V_{CNT} for larger SiO₂ thickness in the range of $50 \text{ nm} < T_{\text{SiO}_2} < 1 \mu\text{m}$.

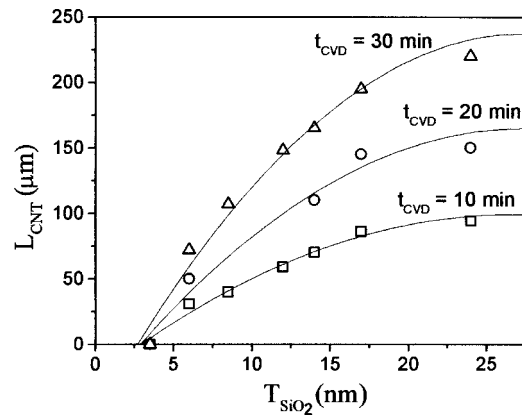


FIG. 3. The CNT length plotted as a function of T_{SiO_2} for different CVD time intervals (t_{CVD}).

cally with SiO₂ thickness. The constant CNT growth rate for a given T_{SiO_2} value suggests that the CNT growth is limited by interfacial reaction. These features are also seen in Fig. 4(b), which is a plot of the CNT growth velocity V_{CNT} vs T_{SiO_2} . We note that V_{CNT} saturates for $T_{\text{SiO}_2} \sim > 50 \text{ nm}$.

Based upon the earlier results, we propose the following mechanism to explain the effect of SiO₂ thickness on CNT growth. Fe from ferrocene diffuses through SiO₂ layers thinner than $\sim 5 \text{ nm}$ and reacts with the Si substrate, leading to the formation of FeSi₂ and FeSiO₄—neither of which catalyze CNT growth—as reported recently.¹⁸ Thus, there is no CNT growth for $T_{\text{SiO}_2} < 5 \text{ nm}$. However, increasing T_{SiO_2} from ~ 6 to 24 nm limits Fe diffusion through SiO₂, and

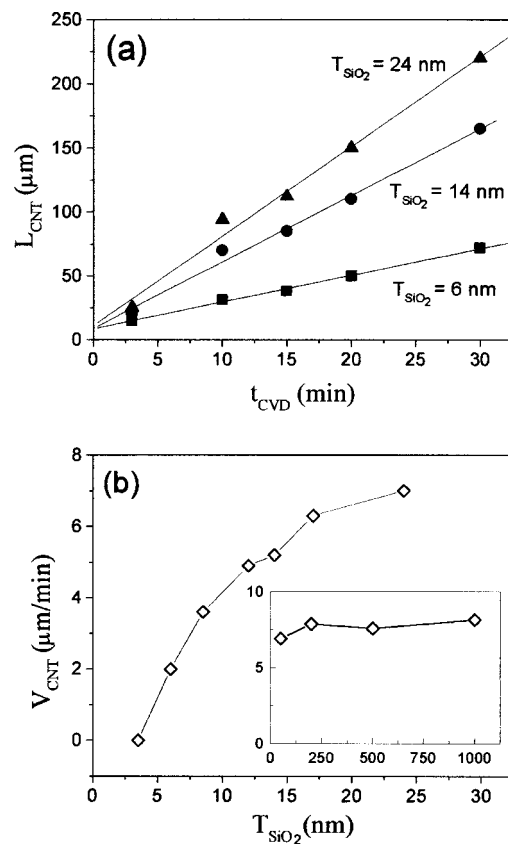


FIG. 4. Plots of (a) L_{CNT} vs t_{CVD} for different SiO₂ thicknesses, and (b) the CNT growth rate V_{CNT} vs T_{SiO_2} . Inset in (b) shows V_{CNT} for larger SiO₂ thickness in the range of $50 \text{ nm} < T_{\text{SiO}_2} < 1 \mu\text{m}$.

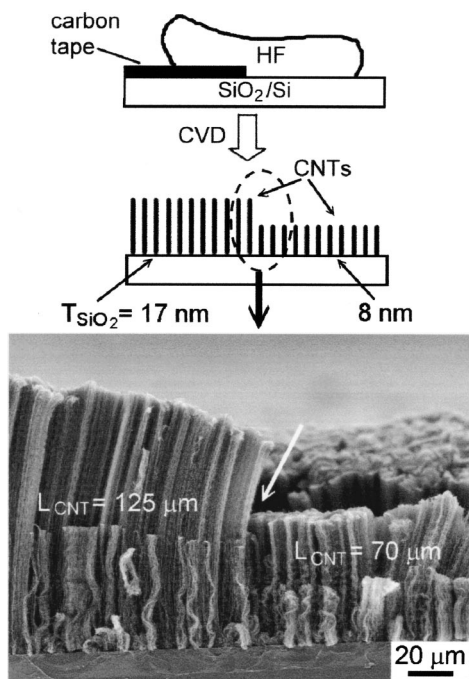


FIG. 5. Schematic sketch illustrating the creation of adjacent regions with different T_{SiO_2} , and subsequent CVD growth of nanotubes. The SEM image shows two CNT layers with lengths of ~ 125 and $70 \mu\text{m}$, respectively. The central white arrow points to the interface separating the regions of different T_{SiO_2} .

promotes the retention of $\gamma\text{-Fe}$, which is conducive for seeding CNT growth. This inference is supported by the presence of a high density of $\gamma\text{-Fe}$ catalyst particles at the CNT– SiO_2 interface.¹⁸ For $T_{\text{SiO}_2} > 50 \text{ nm}$, Fe diffusion into Si is effectively blocked, and hence, produces no further changes on CNT growth rate, as shown in Fig. 4(b).

The constant growth rate for a given T_{SiO_2} in the time scales we investigated indicates that the CNT growth is primarily controlled by the reaction rate of carbon atoms on $\gamma\text{-Fe}$ —i.e., reaction limited, and that the diffusion of carbon clusters decomposed from xylene through the CNT film to the interface is very fast. The highly porous structure of CNT films is believed to allow the carbon precursor to access CNT roots readily. We can thus describe CNT growth by an expression of $V_{\text{CNT}} = C_0 k_s / N$,¹⁹ where C_0 is the carbon concentration at the CNT growth front (the nanotube roots), N is the number density of carbon atoms in the CNT films, and k_s is the reaction rate constant for CNT growth. Since the CVD conditions and the density of CNTs are identical in our experiments, C_0 and N are the same for all the CNT samples. Thus, altering the SiO_2 thickness essentially changes k_s due to the partial modification of catalyst particles on the SiO_2 surface, which results in different CNT growth rates as shown in Figs. 3 and 4.

We can harness SiO_2 thickness-dependent nanotube growth rates to build multilayered CNTs, e.g., with predefined tube lengths in each layer, in a single CVD process. To demonstrate this, we carried out CVD for 20 min on a substrate with two different SiO_2 thicknesses in close proximity. We partially covered a substrate of 17-nm-thick SiO_2 layer with carbon tape, and decreased the thickness of exposed SiO_2 to $\sim 8\text{--}9 \text{ nm}$ by etching it with 10% HF, fol-

lowed by an immediate deionized water rinse. Figure 5 illustrates the template creation process and a SEM image of the as-grown CNTs near the interface between carbon tape-protected portion and uncovered area. We observe two CNT films with two distinct lengths of ~ 125 and $70 \mu\text{m}$, respectively, grown simultaneously on either side of the interface. This result elucidates that SiO_2 -dependent CNT growth offers promise for creating multilayered and 3D architectures by implementing our CVD process on lithographically chiseled patterns with multiple SiO_2 thicknesses.

In summary, we have described the SiO_2 thickness-dependent CNT growth by conventional CVD using xylene and ferrocene as the precursor. A minimum SiO_2 thickness of $\sim 5\text{--}6 \text{ nm}$ is necessary to obtain aligned CNTs. For SiO_2 thickness up to 24 nm, the CNT growth rate and length increase monotonically with SiO_2 thickness. The inhibition of CNT growth at low SiO_2 thickness is explained by partial deactivation of catalyst particles due to their reaction with the Si substrate. Substrate thickness-dependent CNT growth offers promise for fabricating 3D architectures in a single CVD process.

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