Electric-field-directed growth of aligned single-walled carbon nanotubes

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Electric-field-directed growth of single-walled carbon nanotubes by chemical-vapor deposition is demonstrated. The field-alignment effect originates from the high polarizability of single-walled nanotubes. Large induced dipole moments lead to large aligning torques and forces on the nanotube, and prevent randomization of nanotube orientation by thermal fluctuations and gas flows. The results shall open up possibilities in directed growth of ordered molecular-wire architectures and networks on surfaces. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1415412]

Single-walled carbon nanotubes (SWNTs) are molecular wires exhibiting interesting and useful electrical properties,[1] and may be utilized for future generations of integrated molecular electronic devices. A prerequisite for such integration is the ability to assemble individual SWNTs into desired architectures by placing them at specific locations with controlled orientations. We have demonstrated several chemical-vapor deposition (CVD) methods to assemble nanotubes into organized structures by patterned growth approaches.[2–7] Here, we exploit applying external driving forces to direct the growth of SWNTs during CVD. Electric fields have been exploited to manipulate both SWNTs and multiwalled carbon nanotubes (MWNTs). With postgrowth materials, SWNTs aligning with electric fields in liquids[8–10] and vacuum[11] have been observed. However, postgrowth manipulation and assembly of SWNTs have not been very successful thus far due to poor SWNT solubility in liquids and insufficient nanotube purity. Electric fields have been used to manipulate the growth direction of MWNTs previously,[12] but not for SWNTs.

An important step in our field-directed SWNT growth approach involves rational design of the substrate (Fig. 1). (i) First, a 3-μm-thick poly-silicon (poly-Si) film was grown on a quartz wafer [Fig. 1(a)]. (ii) The poly-Si film was then patterned by photolithography and plasma etching to form three parallel trenches in the poly-Si film [Fig. 1(b) shows the cross-section view of the substrate]. The widths of the trenches were varied in the range of 10–40 μm. The widths of the two middle poly-Si lines were 5 μm, and the widths of the two outer poly-Si pads were ~0.5 cm. (iii) A liquid-phase catalyst precursor film was transferred onto the top of the poly-Si pattern by contact printing using a poly(dimethylsiloxane) elastomer stamp[6,7] [Fig. 1(c)]. The sample was then calcined at 300 °C for 12 h in air to remove organic components, resulting in catalyst nanoparticles supported on mesoporous alumina frames on the elevated poly-Si structures.[6,7] (iv) The substrate was mounted on a specially designed insulating ceramic fixture with two metal leads clamped onto the outer poly-Si pads, and placed into the CVD system for SWNT growth. During CVD, a dc (0–200 V) or ac (30 MHz, 10 V peak-to-peak) voltage was applied to the outer macroscopic poly-Si electrodes by using electrical feedthroughs. Electric fields were established across all of the three trenches, as the overall poly-Si structure consisted of three capacitors in series. SWNTs were grown at 900 °C in the flow of methane (500 sccm) mixed with hydrogen (200 sccm) for 4 min in a 1 in. tube furnace. Scanning electron microscopy (SEM) was used to examine the alignment of SWNTs grown in the electric fields. In order to clearly image SWNTs suspended over the trenches, we deposited 5 nm of titanium followed by 15 nm of gold on the sample prior to SEM.

Quartz is chosen as the substrate because of its excellent electrical insulation at high temperatures. Poly-Si is chosen as the electrode material since it is electrically conducting at high temperatures and can be easily patterned by standard processes. Further, poly-Si retains its structural integrity at high temperatures without aggregation.

The SWNTs grown under zero-applied electric field in a control experiment exhibit no preferred orientation and appeared randomly suspended over the trenches [Fig. 2(a)]. In contrast, nanotubes grown under bias voltages of 5 and 10 V [Figs. 2(b) and 2(c), respectively] exhibit good alignment

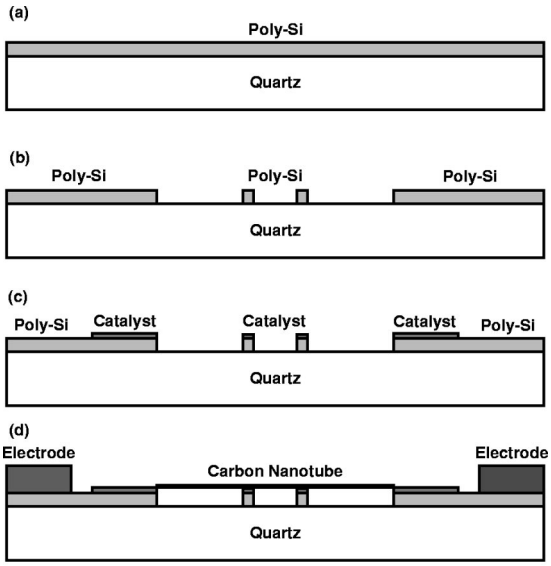

FIG. 1. Schematic diagram process flow for electric-field-directed growth of SWNTs.

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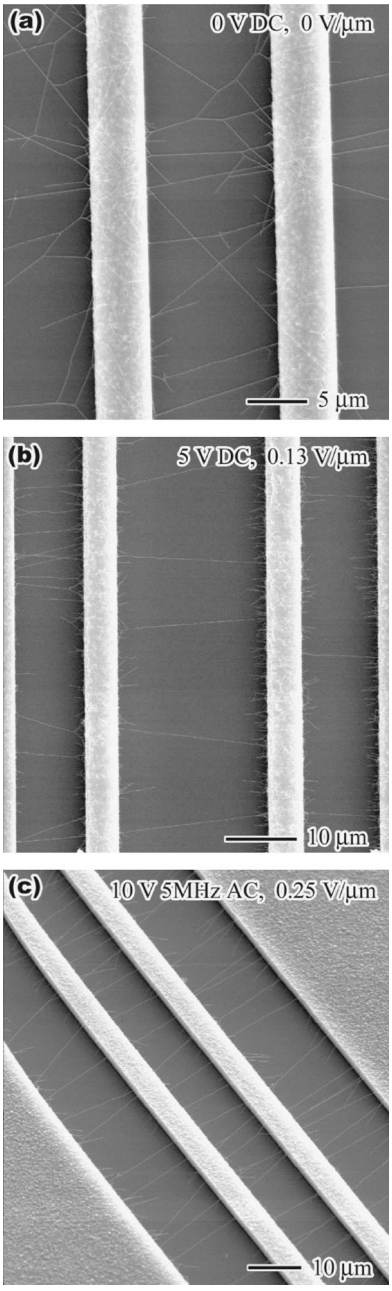

FIG. 2. SEM images of suspended SWNTs grown in various electric fields. The spacing between the edges of the outer poly-Si electrodes is 40 μm.

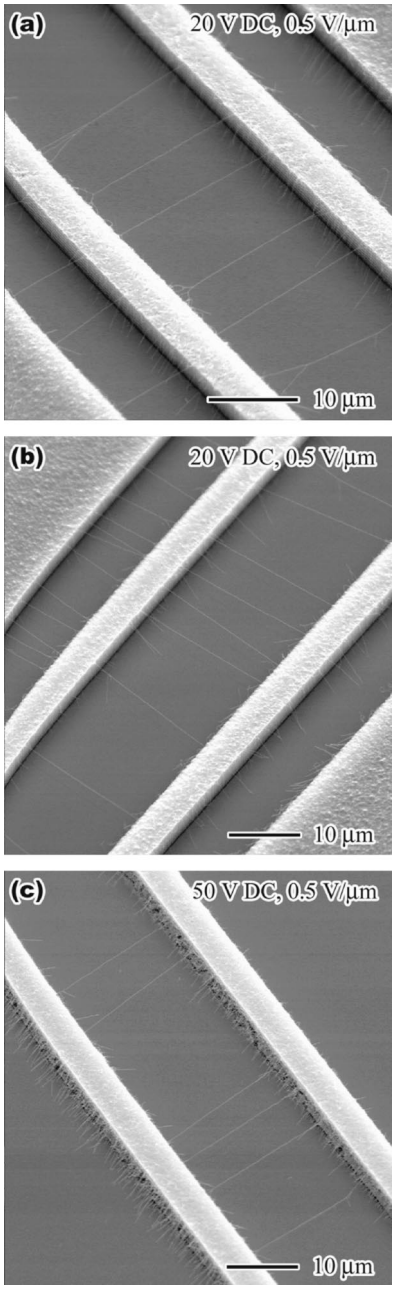

FIG. 3. SEM images of suspended SWNTs grown in various electric fields. The spacing between the outer poly-Si electrodes is 40 μm in (a) and (b), and 100 μm in (c).

along the electric-field direction. In this relatively low voltage (10 V) and field (0.1–0.25 V/μm) regime, we have used both dc and ac fields to direct the growth of SWNTs and obtained similar results.

Highly aligned suspended SWNTs can be grown under electric fields in the range of ~0.5–2 V/μm (bias voltages ~20–200 V). Typical growth results obtained under such conditions are shown in Fig. 3, in which long (>10 μm) SWNTs well aligned along the electric-field direction are clearly observed. For electric fields exceeding ~3 V/μm, we typically observed arcing between the poly-Si electrodes during growth due to electric discharge. The optimum electric fields for directed growth of suspended SWNTs were in the range of 0.5–2 V/μm.

To rationalize SWNT alignment with electric fields, we consider the dipole moment $\mathbf{P}=\alpha\mathbf{E}$ of a SWNT (length $=L$) induced by an applied field of $\mathbf{E}$ (Fig. 4). The static polarizability tensor α of a long SWNT is highly anisotropic.[13] The polarizability along the tube axis $\alpha_{\parallel}$ is much higher than that perpendicular to the tube axis ($\alpha_{\perp}$). For metallic SWNTs, Benedict and co-workers found that $\alpha_{\parallel}$ per unit length diverges, resulting in infinite dipole moments in electric fields. For semiconducting SWNTs, $\alpha_{\parallel}\propto R/E_g^2$, where R and E_g are the radius and band gap of the nanotube, respectively.[13] Recently, Devel derived $\alpha_{\parallel}=4\pi\varepsilon_0(0.25R+1.9)L^2$ (R, L in units of Å) for both metallic and semiconducting SWNTs.[14] Due to thermal activation at our high growth temperature, significant free carriers should exist in the semiconducting SWNTs ($K_BT/E_g\sim 0.2$). Therefore, we apply the theoretical result of Devel to analyze our electric-field-directed growth of SWNTs.

We consider a SWNT grown from an elevated poly-Si

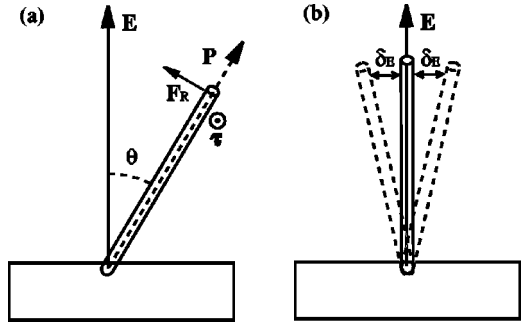

FIG. 4. (a) Diagram showing a SWNT in an electric field. (b) Vibration of a SWNT in an electric field.

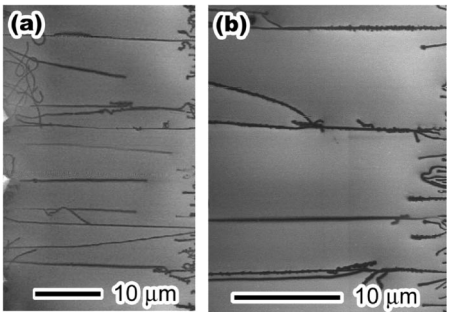

FIG. 5. SEM images of SWNTs (dark lines) at the bottom of the trenches grown under an applied dc voltage of 50 μm. The spacing between the outer poly-Si electrodes is 100 μm.

structure and extending into a trench. For a nanotube oriented at an angle θ with respect to **E** (Fig. 4), unless for θ close to 90°, the dipole moment of the nanotube is along the tube axis with $P=\alpha_{\|}E\cos\theta$. The torque on the dipole moment is $\tau=|\mathbf{P}\times\mathbf{E}|=\alpha_{\|}E^2\sin\theta\cos\theta$. Correspondingly, the force applied on the dipole to rotate and align the tube with **E** is $F_R=\alpha_{\|}E^2\sin\theta\cos\theta/L$ [Fig. 4(a)]. For a SWNT with $L=20\,\mu$m in an applied field of $E=1\,\mathrm{V}/\mu\mathrm{m}$, the torque is $\tau=0.02\sin\theta\cos\theta$ (in nN μm) and the aligning force is $F_R=1.0\sin\theta\cos\theta$ (in μN). For a SWNT oriented along **E** with one end fixed and the length floating, thermal fluctuation could randomize its orientation. It is interesting to note that in the absence of an electric field, the thermal vibration amplitude of the floating end of a SWNT is $\delta=\{0.846L^3KT/[YdG(d^2+G^2)]\}^{1/2}\propto L^{3/2}$,[15] where $T=1173\,\mathrm{K}$, $Y=1.0\,\mathrm{TPa}$ is the Young's modulus, $d=2R=2$ nm is the diameter, and $G=0.34$ nm is the van der Waals distance in graphite. This gives rise to a staggering thermal vibration of $\delta\sim6.3\,\mu$m for a $L=20\,\mu$m tube at the growth temperature (900 °C). In an electric field, however, the vibration amplitude of the free end of the SWNT is $\delta_E\approx L[K_BT/U_E]^{1/2}=L[K_BT/(\alpha_{\|}E^2)]^{1/2}$, which is proportional to $1/E$ and independent of L (due to $\alpha_{\|}\sim L^2$. $U_E=\alpha_{\|}E^2$ is the potential energy of the nanotube dipole when aligned with **E**). For a SWNT with $R\sim1$ nm and $L=20\,\mu$m, the thermal vibration amplitude of its free end is only $\delta_E\sim0.57\,\mu$m in a field of 1 V/μm, significantly smaller than the length of the tube, indicating negligible thermal randomization of the SWNT alignment from the electric field (the physics here somewhat resembles that for a pendulum whose thermal vibration amplitude decreases under high gravity). For weaker fields (e.g., $E\sim0.1\,\mathrm{V}/\mu\mathrm{m}$), $\delta_E(\sim5.7\,\mu\mathrm{m})$ becomes a substantial fraction of L, which could result in poor alignment with the field. These analyses are consistent with the experimental finding that for $E\sim0.1$–$0.2\,\mathrm{V}/\mu\mathrm{m}$, the degree of SWNT alignment is not as good as for $E\sim0.5$–$2\,\mathrm{V}/\mu\mathrm{m}$.

Another factor that could randomize the orientation of SWNTs is gas flow in the CVD system. However, we found this factor was negligible in our present setup. SWNTs were aligned with the electric-field direction and perpendicular to the gas flow.

We also used SEM to image the SWNTs grown from elevated poly-Si structures and landed on the bottom quartz substrate. In this case, SEM was carried out without coating the samples with metal. We found that most of the SWNTs resting on the flat quartz substrate in the trenches were also aligned with the electric-field direction (Fig. 5). The insulating quartz substrate appeared as a bright background due to electrical charging, and the SWNTs appeared as dark lines[4] (Fig. 5). In control experiments, we placed a catalyst on a flat quartz surface and carried out CVD growth with electric fields applied across the surface. Most of the SWNTs grown were not aligned along the electric-field direction. This is because SWNTs grown on a flat surface can easily contact the substrate. Strong van der Waals interactions with the substrate will hold the nanotube in place, preventing its response to the electric field.

In summary, we have demonstrated electric-field-directed growth of SWNTs. To fully utilize the electric-field alignment effect, it is important to keep SWNTs from van der Waals interactions with nearby surfaces during growth. Our approach shall allow building complex ordered SWNT structures by directed growth, and integrating them for molecular electrical, mechanical, and electromechanical devices.

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