Electric-field-aligned growth of single-walled carbon nanotubes on surfaces

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Aligned single-walled carbon nanotubes are grown onto the surfaces of SiO$_2$/Si substrates in electric fields established across patterned metal electrodes. Calculations of the electric field distribution under the designed electrode structures, the directing ability of electric fields, and the prevention of surface van der Waals interactions are used to rationalize the aligned growth. The capability of synthesizing oriented single-walled nanotubes on surfaces shall open up many opportunities in organized architectures of nanotubes for molecular electronics. © 2002 American Institute of Physics. DOI: 10.1063/1.1518773

Obtaining organized single-walled carbon nanotube (SWNT) structures is a critical step towards interesting and practical devices of novel molecular wires. With two approaches—post-growth assembly and in situ controlled growth—progress has been made to reach this goal. In both approaches, electric fields have been exploited to control the orientation of SWNTs, utilizing the highly anisotropic polarizability of nanotubes. In situ growth by chemical vapor deposition (CVD) in an electric field can direct the orientation of SWNTs, as shown by our group with the nanotubes in suspended form.

While suspended SWNTs with directionality are important to mechanical and electromechanical studies and devices, it is equally important to grow aligned nanotubes resting on surfaces. This ability will then allow successive patterned growth steps in electric fields to produce multiple sets of nanotubes aligned to various directions, and allow metallization and other integration steps to fabricate addressable devices, without the mechanical instability problems of suspended nanotubes. Here, we show that aligned SWNTs on surfaces can indeed be obtained by electric-field-directed CVD growth, with a rational choice of substrates, electrode materials, and structures. The mechanism for alignment involves suitable electric field distributions and the prevention of van der Waals binding with substrate surfaces during nanotube growth.

We started with Si wafers with 1.85-$\mu$m-thick thermally grown SiO$_2$ as substrates. We used molybdenum metal electrodes to establish electric fields on the substrates, as shown in Fig. 1(a). The electrodes were patterned by photolithography and liftoff, each with a dimension of 0.8 cm by 0.3 cm and a thickness of either 50 or 100 nm. The gap between the Mo electrodes was 10 $\mu$m. We then patterned a catalyst on top of the two opposing Mo electrodes using a second photolithography step aligned to the electrodes. The catalyst regions on the two electrodes were designed to be 5 $\mu$m x 0.4 cm strips containing an alumina supported Fe/Mo catalyst, and were ~3–5 $\mu$m away from the edges of the Mo electrodes [Fig. 1(b)]. The catalyst patterning step utilized a poly(methylmethacrylate) (PMMA) and photoresist double layer approach. The top photoresist layer was first patterned by standard photolithography. After developing, oxygen plasma was used to etch into and form wells in the PMMA. The top photoresist layer was then fully removed by exposure to a high flux of light and subsequent development. Catalyst material was then deposited from a methanol suspension into the patterned PMMA wells followed by liftoff in acetone. We used the double layer approach so that PMMA can be patterned by standard photolithography and photomasking.

FIG. 1. Structure of samples used for electric field aligned growth of SWNTs on surfaces. (a) Cross-sectional view of the Si/SiO$_2$ (1.85-$\mu$m-thick) substrate, microfabricated Mo electrodes, and the catalyst strips (not to scale). (b) An optical image showing the top-view of a sample. (c) Electric field distribution and equipotential lines calculated for the left and right Mo electrodes biased at 10 and 0 V, respectively. The underlying Si substrate is floating. The lengths of the field line arrows scale with the strengths of the local fields.
dry etching. The photoresist pattern itself was not used for catalyst patterning due to the incompatibility of photoresist with methanol.

Aligned SWNTs across the gap between the electrodes were grown in a 1 in. CVD system equipped with electrical feedthroughs. The substrate was mounted on a home-made fixture on which two metal stainless steel clips were designed to make electrical contact to the Mo electrodes for applying bias voltages (~3–20 V) across the gap. The Si substrate underlying the SiO$_2$ layer was kept floating. A 40 kΩ serial resistor was used to limit the current. SWNTs were grown at 900 °C for 2 min under 720 mL/min of methane, 500 mL/min of hydrogen, and 12 mL/min of ethylene flow. Pure hydrogen was flown during heating and cooling the CVD system to prevent oxidation of the Mo electrodes by possible oxygen impurities.

The substrates used in the current work were SiO$_2$/Si wafers (instead of quartz used previously for aligned suspended SWNTs$^3$). The 1.85-μm-thick thermally grown SiO$_2$ layer was found stable against electrical breakdown under 3–20 V applied across the Mo electrodes. Mo was used for electrodes in place of polysilicon, due to its compatibility with high temperature CVD growth conditions without loss of conductivity.$^8$ These substrate and electrode materials significantly facilitated the current work owing to their simplicity and ease of microfabrication.

Control experiments reveal that, in the absence of electric fields, nanotubes grown from the catalyst regions bridge the electrodes in random orientations, as shown in the atomic force microscopy (AFM) images in Fig. 2. In strong contrast, high degree of alignment is observed for nanotubes grown under applied electric fields between the Mo electrodes. Figure 3 shows AFM data recorded with samples grown by CVD with a 10 V bias voltage applied across the 10 μm gap between the electrodes. The nanotubes are clearly aligned perpendicular to the edges of the electrodes, in the direction of the electric field. Scanning electron microscopy (SEM) imaging has also revealed aligned nanotube structures along the electric field direction (Fig. 4). We have carried out nanotube growth under applied voltages of 3, 5, 10, and 20 V. Alignment appears to be less effective, although still present, when 3 V is applied across the 10 μm gap. On the other hand, no obvious improvement is observed in the alignment of nanotubes when the voltage is increased to 20 V. Further increase in voltage tends to break down the SiO$_2$ dielectric.

FIG. 2. Random orientations of nanotubes grown by CVD when no electric field is applied in a control experiment. The two AFM images show randomly oriented nanotubes in the gap region between the Mo electrodes. The edges of the Mo electrodes are shown at the top and bottom of each image.

FIG. 3. Aligned nanotubes resting on SiO$_2$ surfaces after electric field directed growth. The four images were obtained with different samples that had gone through independent electric-field-directed growth runs. The nanotubes show clear alignment in the direction of the electric field, perpendicular to the edges of the Mo electrodes.
FIG. 4. An SEM image of aligned nanotubes grown by CVD in an electric field. The dark lines in the center region of the image are aligned nanotubes. The nanotubes and the Mo electrodes (regions bridged by the nanotubes) appear dark since they are electrically conducting, whereas the SiO$_2$ surface in the gap region appears bright due to charging effects under our imaging conditions. The catalyst strips are visible as the top and bottom bright areas.

layer. Thus, we identify that ~10 V applied between the electrodes spaced at 10 μm is optimum for aligned growth of nanotubes on surfaces. Using this condition, we have carried out growth with 20 samples, and observed a reproducible and consistent electric field alignment effect, with only slight variations in the degree of alignment from sample to sample.

To understand the alignment of nanotubes resting on SiO$_2$ surfaces, we first calculate the electric field distribution for our sample geometry using the MEDICI simulation program (by Avant! Co.) to solve the Laplace equation numerically. Fig. 1(c) shows a cross-section view of electric field vectors and equipotential lines for the sample structure. At the locations of the catalyst strips from which the nanotubes are grown, the electric field is nearly perpendicular to the Mo metal surface, with a field strength of ~0.5 V/μm. Right in the middle of the gap between the two metal electrodes, the electric field is 0.2 V/μm at the SiO$_2$–air interface. Note that the field lines in the gap are not perfectly parallel to the surface plane in the immediate vicinity of the surface, but are at a small angle. This is caused by the distortion effect of the floating Si substrate underneath the oxide layer.

We suggest that nanotubes grown from the catalyst regions initially extend into the air nearly normal to the metal electrode surface, along the direction of the local electric field. The nanotubes follow the electric field lines as they lengthen, and with the existence of field gradients, they tend to follow the field lines with the highest strength to maximize the interaction between the electric field and the induced dipole moments on the nanotubes. When the nanotubes are over the electrode gap region, they are aligned to the overall field direction in the gap (perpendicular to the electrode edges on the x–y plane), become directed towards the substrate by field gradients, and subsequently fall onto the surface. This results in aligned nanotubes immobilized on the surface by van der Waals forces.

There are two important factors for the aligned growth of SWNTs onto substrates. The first is the directing or aligning ability of the electric field. In our previous work, we have shown that in a field of ~1 V/μm, the induced dipole (~10$^6$ Debye, largely along the tube axis due to the strong anisotropy in polarizability) on a ~10 μm long SWNT is sufficient to overcome most of the orientation randomizing forces such as thermal vibration. This condition is satisfied here since the electric field strength is on the order of 1 V/μm. An equally important factor is that during growth and lengthening, the nanotubes must stay away from surfaces to avoid capture by the surfaces, so that the nanotubes can fully experience the aligning effect of the electric field. For a nanotube pinned on a surface, strong van der Waals interactions will prevent it from responding to the field directing effect. This condition is also satisfied by our sample design, as the nanotubes grown from the catalyst regions do not contact the substrate until they have been fully aligned to the electric field and guided onto the substrate.

A control experiment was carried out with the same substrate and electrode structures, but different catalyst locations. We placed catalyst, in the form of discrete Fe$_3$O$_4$ nanoparticles, onto the SiO$_2$ surface in the gap region between the two Mo electrodes, and carried out CVD growth under a 10 V applied voltage across the 10 μm gap. The orientations of nanotubes thus grown appear random on the surface without any apparent alignment to the electric field direction inside the gap. We attribute this to the fact that the electric field direction is not normal to the surface at the catalyst sites in the gap region, and that field gradients in this region do not favor nanotubes directing away from the surface. Thus, once reaching a certain length at the early stage of growth, the nanotubes touch the substrate and become pinned.

In summary, we have used in situ electric fields to grow aligned SWNTs onto surfaces by CVD. Excellent alignment of nanotubes is obtained on SiO$_2$/Si surfaces based on a rational choice of materials and sample structure design. These results could lead to the synthesis of complex organized nanotube structures for molecular electronics applications.

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