

Oriented growth of single-wall carbon nanotubes using alumina patterns

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Abstract

We present a new technique for controlling the orientation of single-wall carbon nanotubes grown by chemical vapour deposition. The technique involves prior patterning of alumina islands on oxidized silicon substrates. Nanotubes growing on the oxide near an alumina boundary are oriented perpendicular to the boundary. Field-effect transistors were successfully fabricated from nanotubes produced using this technique. We argue that the orientation is caused by an electric field due to space charge associated with the alumina.

1. Introduction

Single-wall carbon nanotubes for electronic device applications are commonly grown by chemical vapour deposition (CVD) on oxide substrates such as silicon dioxide (SiO₂). This process normally produces nanotubes with random position, length, orientation and wrapping vector (which determines the band structure). In order to improve the yield and quality of nanotube devices, for applications including field-effect transistors [1–3], sensors [4, 5], and studies of electrons in one dimension [6], the search is on for effective techniques to control these parameters. Various degrees of control of the orientation have been obtained by using crystalline surfaces [7], by magnetic orientation of the catalyst particles [8], by growing from porous silica templates [9], and by electric field alignment [10–12]. In the last technique, which has attracted the most attention to date, an electric field is produced near the substrate, during the CVD growth, by a voltage bias applied between metallic electrodes patterned on the sample.

In this paper we introduce a new method for controlling nanotube orientation on a scale of approximately 50 μm. This method consists of patterning alumina (Al₂O₃) features on an oxidized silicon substrate prior to nanotube growth. This technique is simple and flexible. It requires a single lithography step, which is compatible with other fabrication procedures, and it does not require electrical leads to be connected into the CVD furnace.

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2. Sample preparation

The sample preparation is summarized in figure 1. Alumina features are first patterned on a clean substrate (400 nm of thermal SiO₂ on *n*⁺⁺⁺ Si, resistivity 0.001–0.005 Ω cm) by optical lithography. Approximately 6 nm of alumina is deposited in an electron-beam evaporator (using either an aluminium (Al) target with a background pressure of 10⁻⁵ Torr or an alumina target with 10⁻⁶ Torr) on top of the developed resist pattern (Clariant, AZ1512). The alumina is then lifted off in acetone. The catalyst is prepared by sonicating Fe(NO₃)·9H₂O (Sigma-Aldrich) in IPA. A concentration of about 1 μg ml⁻¹ results in an appropriate density of non-overlapping nanotubes. The solution is dropped onto the sample, which is then blown dry. Nanotube growth [13] is carried out at 900 °C in a 1" tube furnace in hydrogen (H₂) and methane (CH₄) (typical flow rates are 400 and 500 sccm respectively). Note that at higher total gas flow rates (for example, 1500 sccm) the flow has a significant effect on nanotube orientation, as we discuss below. Finally, to make simple devices metal electrodes are subsequently patterned with optical lithography (figures 1(c) and (d)), as described below.

3. Results and discussion

Our main results are illustrated by the images in figures 2 and 3. The scanning electron microscope (SEM) images in figure 2 show that nanotubes located on the SiO₂ near the boundaries of alumina features are oriented approximately perpendicular

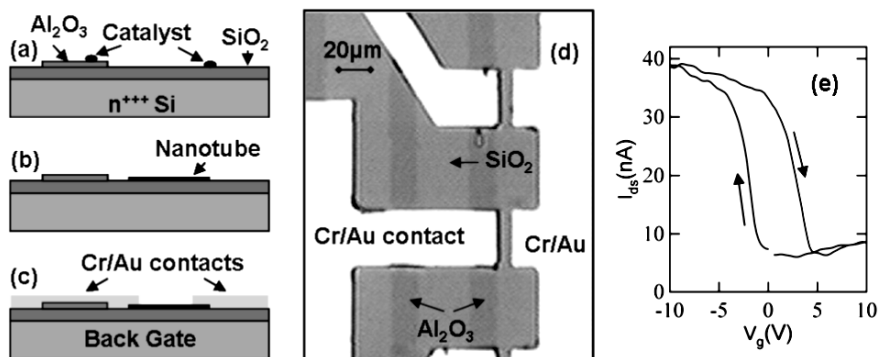


Figure 1. Sample preparation and characterization: (a) schematic cross-section showing the metallic silicon substrate with a thermal oxide, on which 6 nm-thick Al_2O_3 and then catalyst were deposited. (b) A carbon nanotube has grown on the oxide close to the alumina. (c) Cr/Au electrodes are deposited. HF etching of exposed Al_2O_3 is performed at this stage (not shown). (d) Optical microscope image of a fabricated device. (e) Current versus gate voltage (applied to the Si substrate) of a fabricated device (using $V_{ds} = 25$ mV). The arrows indicate the direction of the gate sweep.

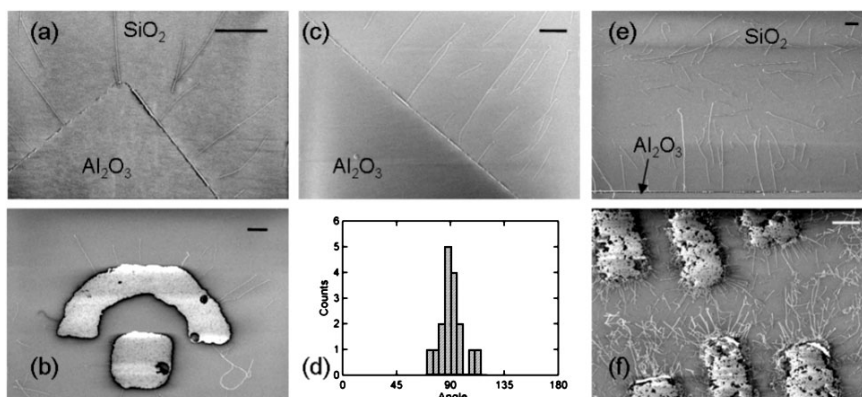


Figure 2. SEM images showing nanotubes grown in the neighbourhood of alumina islands. (a)–(c) Nanotubes growing near alumina boundaries of various geometries. (d) Histogram of angles between nanotubes and the alumina edge. (e) The orientation zone extends to about $50 \mu\text{m}$. (f) Results obtained at high catalyst concentration. Scale bars in SEM images are $10 \mu\text{m}$.

to the closest boundary. This remains true even when the alumina island has a rectangular corner (figure 2(a)) or a more complex shape, even with rough edges (figure 2(b)). When the boundary is long and straight, and far from any other boundary, the orientation effect is very uniform, as seen in figure 2(c). Figure 2(d) is a histogram of angles between the nanotube axes and the boundary, showing a narrow distribution centred at 90° . Orientation occurs in a belt $30\text{--}50 \mu\text{m}$ wide adjacent to the alumina. Nanotubes on the rest of the SiO_2 surface grow with no preferred orientation, or in some cases oriented by the gas flow, as can be seen in figure 2(e). If the density of nanotubes is too high they tend to overlap and entangle, degrading the orientation effect, but nevertheless the influence of the alumina can still be seen (figure 2(f)). Atomic force microscope images, such as in figure 3, show that the oriented nanotubes are of a quality similar to those grown without alumina, with diameters ranging between about 1 and 4 nm.

We have established that this orientation technique is compatible with the fabrication of nanotube devices. To do so, we used an alumina pattern comprised of an array of strips $20 \mu\text{m}$ wide and $40 \mu\text{m}$ apart (see figure 1(d)). Following nanotube growth, metal contacts (100 nm Au on 5 nm Cr) were fabricated using a second optical lithography step aligned to the alumina strips. Finally, a brief etch in hydrofluoric acid was used to remove the alumina which was not covered by

metal. This last step was necessary as the alumina lines were found to become electrically conducting after growth, probably due to carbon deposition. The electrical characteristics of the resulting devices, under ambient conditions, were similar to those of devices we prepared using a standard process without alumina. An example is shown in figure 1(e). The metallically doped silicon substrate was used as the gate electrode. The hysteresis seen here is common to semiconducting nanotube devices [15]. The fact that the conductance does not go to zero at positive gate voltage can be attributed to the presence of several nanotubes, both metallic and semiconducting, connected in parallel.

We now consider the mechanism behind it. In fact, there are several clues to its origin. First, we note that many of the tubes appear to have a ‘hook’ shape at one end (see figure 2(c)). This is a common, though not universal, feature of the CVD growth. We observe that the oriented nanotubes nearly always have a hook at the end furthest from the alumina. To investigate the origin of the hooks, we performed CVD growth on clean SiO_2 substrates at high gas flow rates (500 sccm hydrogen and 1000 sccm methane), which are sufficient to produce rough alignment of most nanotubes with the flow direction (figure 4). Interestingly, we note that most of the nanotubes grown this way have hooks at their upstream ends. We are led to a picture in which the hook occurs at the ‘root’ of the nanotube,

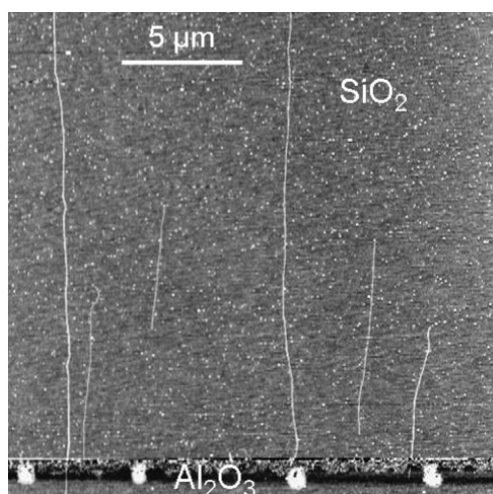


Figure 3. AFM image of aligned nanotubes next to an alumina pad (bottom).

which is fixed to the substrate while the other end is dragged downstream. This ‘hook–root’ picture is consistent with the following simple model: the nanotube grows almost rigidly away from the substrate from its root, but its free end is pulled downstream, while oscillating due to thermal fluctuations. When at some point a part of the nanotube touches the substrate it sticks, and van der Waals attraction then zippers the nanotube down to the substrate, leaving a small curved region near the root. The size of this hook is thus determined by the van der Waals force, the nanotube’s stiffness, and the direction of the root growth. This model however remains to be confirmed.

Seeing that the hook indicates a fixed root, we deduce that the nanotube free ends are somehow drawn towards the alumina. We can rule out drag by local gas flow as a cause since the orientation responds to even complex alumina boundaries (figures 2(a), (b)). The two remaining alternative forces are magnetic and electric. We can conceive of no magnetic force mechanism that would be sensitive to the alumina boundary and have a significant magnitude. On the other hand, a large electric field may be created by surface charging in the hot, reactive conditions of the CVD growth, and/or by an unbalanced charge at the alumina/oxide interface. Negative fixed charge densities as high as $\sim 6 \times 10^{12} e \text{ cm}^{-2}$ have been detected previously at such interfaces [14], which gives an idea of the order of magnitude of the net charge that may be present.

Orientation of single-wall nanotubes during CVD growth by externally applied electric fields is a well-established phenomenon [10–12]. In the presence of a strong enough field ($\sim 0.2 \text{ V } \mu\text{m}^{-1}$), nanotubes align with the field lines due to their induced dipole moments. Moreover, to explain the observed alignment in [11] it is also necessary to suppose that, in a nonuniform field, the nanotubes are attracted towards a region of higher field intensity [11]. To investigate whether similar mechanisms can explain our results, we consider what the effect would be of a uniform negative space charge, with areal density σ , residing at the alumina/oxide interface. The electric field profile in this model is shown in figure 5.

First, we consider the overall strength of the electric field in this model. The field is proportional to σ , and for a plausible charge density, $\sigma = 1 \times 10^{12} e \text{ cm}^{-2}$, its magnitude decays to

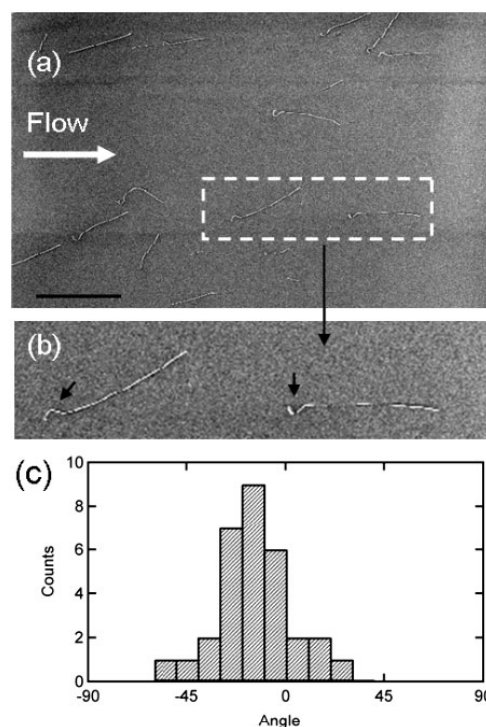


Figure 4. Alignment of nanotubes to gas flow direction during CVD growth: (a) SEM image of nanotubes grown at a high gas flow rate. Scale bar is $10 \mu\text{m}$. (b) Zoom on two nanotubes showing ‘hooks’ indicated by arrows. (c) Histogram of angles of isolated tubes in respect to the approximate gas flow direction.

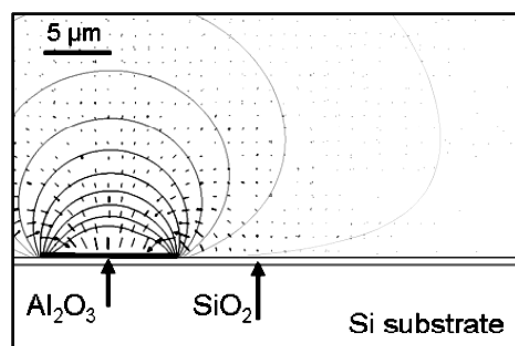


Figure 5. Electric field and potential contours next to a $10 \mu\text{m}$ -wide alumina strip calculated using a finite-element simulation. The spacing of the equipotential lines is 6 V .

$0.1 \text{ V } \mu\text{m}^{-1}$ at $15 \mu\text{m}$ from the boundary. Hence it is strong enough to influence nanotube orientation within approximately this range. Next, we consider the field orientation. The field at the surface is almost perpendicular to the oxide (except very near the alumina). Hence the field will tend to orient a nanotube perpendicular to the substrate as it starts to grow. This may assist growth by reducing its likelihood of the nanotube being captured by the van der Waals interaction with the substrate. Finally, we need to explain the apparent alignment of the nanotubes towards the alumina. Away from the surface, the field lines curve towards the alumina, so as a nanotube lengthens we expect it also to curve somewhat in the same direction as it follows the field lines. We speculate that the free part of the nanotube, undergoing thermal fluctuations, is

on average attracted to the alumina as a result of the increasing field intensity, which decreases its dipole energy. The same principle was invoked to explain why the nanotubes are pulled towards the substrate in [11]. After any part of the nanotube touches the substrate, the van der Waals force pulls it down, leaving a hook at the root, just as in our flow alignment model.

There is additional circumstantial evidence for this electric field model. First, we observe that shorter nanotubes are less reliably oriented than longer ones (as apparent in figures 2(b) and (c)). This can be attributed to their smaller dipole and more limited ability to bend to follow the field lines. Second, we observe that nanotubes almost never grow from the alumina patterns, even though nanotubes are known to grow on substrates uniformly coated with alumina [7] and we deposit the catalyst particles over the entire sample. We hypothesize that opposite direction of the electric field over the alumina caused by the charging effect inhibits the growth of nanotubes while promoting the formation of carbonaceous material.

In the future, we aim to better understand this orientation technique by varying parameters such as the alumina island size, growth conditions, and substrate doping, silicon dioxide thickness. In particular, we expect the field strength will linearly increase with the oxide thickness; thus for thinner oxides we would expect the range of the orientation to be smaller. In this direction, we did perform tests with a very thin oxide (in fact, the native oxide on a silicon wafer), and in that case saw no orientation of the nanotubes, consistent with the model. It would also be interesting to investigate the effectiveness of materials other than alumina.

4. Conclusions

In summary, we have shown that the orientation of single-wall carbon nanotubes grown by chemical vapour deposition on SiO₂ can be controlled by defining alumina features on the SiO₂ substrate. The nanotubes tend to grow towards the alumina. The orientation mechanism appears to be associated with an

electric field created by a charge accumulation associated with the alumina. This technique has been successfully incorporated into the fabrication of nanotube field-effect transistors. We have also demonstrated that high gas flow can be used for rough, large-scale orientation control, and thereby that the hook-like shape often seen at the end of a nanotube occurs at the end rooted to the substrate.

Acknowledgments

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