Top-down approach to align single-walled carbon nanotubes on silicon substrate

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We report controlled horizontal alignment of single-walled carbon nanotubes (SWNTs) directly grown on trench SiO2/Si substrate. The nanotubes were found to align along the trenches, which were created via electron beam lithography followed by reactive ion etching. From the experimental observations, the alignment mechanism was proposed. Furthermore, field-effect transistors fabricated from these substrates showed acceptable mobility and on/off ratio as high as 104. The method offers the possibility of large-scale integrated SWNT electronics for mass production.

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Single-walled carbon nanotubes (SWNTs) have been of interest due to their superior mechanical and electrical properties.1 Applications such as flexible electronics,2 chemical sensors,3 and microelectromechanical devices4 have been demonstrated. In order to fully exploit the superior electronic properties of carbon nanotubes, the growth of horizontally aligned SWNTs on suitable substrates is a critical step for large-scale nanotube-based electronics. Such alignment has been demonstrated on single-crystal substrates such as sapphire (α-Al2O3) and quartz (SiO2).5–8 The proposed mechanism is that SWNTs align on a particular atomic arrangement6 or along the ordered atomic steps after substrate treatment.5,8,9 These results are important for future nanoelectronics applications because the nanotubes’ alignment on a substrate improves the efficiency of device fabrication and enables nanotube integration on circuits. However, subsequent processes like nanotube transfer onto SiO2/Si are still needed to create a more practical electronic application.

On the other hand, SWNT alignment on a SiO2/Si substrate is expected since the current field-effect transistor (FET) configuration is fabricated on a Si wafer with an SiO2 layer. SiO2 plays several important roles in current devices such as an insulator for back-gated transistors, device-to-device isolator, and surface stabilizer. FET based solely on an individual SWNT on SiO2/Si system has long been validated with modest current outputs.10 Multichannel devices are expected to give higher current outputs, which are applicable to the current Si-based devices. It is therefore desirable to realize dense, aligned nanotubes on silicon. The most obvious path for the realization of this device configuration is the transfer of the nanotubes aligned on single crystals.1,11,12 However, this approach is too tedious and possesses an intrinsic possibility for carbon nanotube contamination and deterioration11,12 making it not ideal for large-scale nanoelectronics production. Moving forward, several methods on carbon nanotube alignment directly grown on SiO2/Si were reported,13,14 but may take some time to be practical for mass production due to the low degree of alignment and low density. In this work, we present a new, top-down based approach to align SWNTs on a SiO2/Si substrate by substrate modification. Our method has the potential for large scale-controlled nanotube alignment on silicon.

We first modified our substrate by creating trenches through electron beam (EB) lithography followed by reactive ion etching (RIE). A silicon substrate with 300 nm thermally grown SiO2 was cleaned by sonicating in acetone for 5 min prior to spin coating of positive EB resist (ZEP520A, Zeon Corporation). In EB lithography, different linewidths (100–500 nm) and depths (5–70 nm) were studied with constant spacing (500 nm). The resist was developed using EB developer and subsequently rinsed. The exposed SiO2 was etched by either RIE using CF4 gas (RIE, SAMCO 10iP) or buffered hydrofluoric acid (BHF) treatment. Lastly, the remaining resist was lifted off.

Prior to thermal chemical vapor deposition (CVD) growth of nanotubes, stripe resist patterns positioned perpendicular to the substrate’s trenches were made by photolithography. The substrate was then dipped into aqueous solution containing Fe(NO3)3·9H2O and MoO2(acac)2 with 94:6 molar ratio and subsequently dried at 100 °C before the remaining resist was lifted off.9 Finally, SWNTs were grown at 900 °C for 20 min under mixed CH4 and H2 gases. The Fe–Mo salts decomposed during the CVD forming nanoparticles, which act as the catalyst. Depth and width measurements were done using atomic force microscope (AFM), and the nanotube-FET was made by patterning the source and drain gold (Au) electrodes defined using photolithography.

Figure 1(a) shows a scanning electron microscope (SEM) and AFM images of the parallel trenches with ~36 nm depth created on SiO2/Si surface by RIE. The trench width and spacing are ca. 200 and 500 nm, respectively. Using the patterned Fe–Mo catalyst, carbon nanotubes were grown on this substrate, as shown in Figs. 1(b) and 1(c). We observed that carbon nanotubes align in the direction parallel to the created trenches. It is also seen that nanotubes grow from both ends of the catalyst pattern. To avoid the gas flow-induced alignment observed under a specific condition,13 we set the CH4–H2 gas flow perpendicular to the trench. In the present case, the growth direction was not affected by the gas flow and was solely dependent on the direction of trenches. In Fig. 1(d), the periphery of the pat-
patterned area is indicated. Inside the white border (trenched), the carbon nanotubes were oriented to the trench direction, while outside the border (plain), the nanotubes were randomly oriented. These results clearly show that the trench pattern determines the direction of the nanotube growth. The aligned nanotubes showed a typical Raman spectrum of SWNTs, with radial breathing mode at 100–200 cm\(^{-1}\) and G-band at \(\approx 1595\) cm\(^{-1}\), indicating that the aligned nanotubes are single-walled (Supporting Information).\(^{13}\)

We studied the SWNT growth on different trench structures; the effects of trench depth are shown in Figs. 2(a)–(c). The relatively shallow [\(\approx 15\) nm, Fig. 2(a)] and deep [\(\approx 69\) nm, Fig. 2(c)] trenches gave lower degree of nanotube alignment. We found the trenches with the depth around 25–40 nm reproducibly offered aligned nanotubes. The trenches were also made by wet-etching process using BHF, as shown in Fig. 2(d). To maintain the trench pattern, shallow trenches with \(\approx 6\) nm depth were made because the etching proceeded even underneath the EB resist when BHF was used. Despite of the shallow etching, the partial alignment of nanotubes was observed, but the degree of alignment was low.

Here, we discuss the alignment mechanism of SWNTs on trenched SiO\(_2\)/Si substrates. On plain SiO\(_2\)/Si substrates, the nanotube growth usually occurs based on a base-growth mechanism.\(^{16}\) In the base-growth mechanism, the catalyst remains on the substrate, while the nanotubes slide against the substrate during the growth process. We speculate that the nanotube growth direction was influenced by van der Waals interaction from the substrate surface. Figure 3(a) is an example of a typical carbon nanotube that was aligned in a particular trench. The nanotube was “caught” at position 1 but it “escaped” from the wall and again caught at a different position 2. This “caught-escape-caught” mechanism is frequently observed on all of our processed substrates [see Fig. 1(c)] and the caught part gave the straight tubes aligned along the trench edge. Therefore, we speculate that the side wall of the trench as well as the base plays an essential role in the nanotube alignment, as illustrated in Fig. 3(b). In this case, the angle between the wall and the base is important for the high-degree of alignment. This mechanism may also be responsible for the guided growth on atomically stepped crystal surfaces.\(^{5,9}\) To catch a nanotube with a diameter of 1–2 nm at the trench corner, the trench should have a sharp corner. However, our method of creating trenches do not consistently give us perpendicular surfaces so that nanotubes can escape from the trenches. This was confirmed from the tilted SEM image of our trenched substrate [Fig. 3(c)]. For round trenches, carbon nanotubes will just glide over the trench. The dependence of the nanotube alignment on the
trench structures seen in Fig. 2 could be explained by edge structure of the trenches. For example, the wet-etched [Fig. 2(d)] trenches would have relatively round and smooth corners.

We exploit our findings by making FETs. The device showed a well-behaved transfer curve [Fig. 4(a)] after breakdown of metallic nanotubes.\textsuperscript{17} Making the gate voltage more negative increased the drain current, suggesting a $p$-type behavior [Fig. 4(b)]. The device showed a mobility $\mu$ of $\sim 5$ cm$^2$ V$^{-1}$ s$^{-1}$ (channel length=4.3 $\mu$m, width=19 $\mu$m, and SiO$_2$ thickness=300 nm) using the formula described in the previous paper.\textsuperscript{8} This result does not consider contact effects of the electrodes and may further be increased by choosing the right electrode material.\textsuperscript{18} We have measured more than ten devices and on/off ratio ranges from 10 to 10$^4$ with an average value of 10$^3$ after breakdown. These values are comparable to present studies involving SWNTs on silicon substrate.\textsuperscript{19} We expect these values to increase with denser, more aligned nanotubes.

It has long been considered that the artificially made trenches have smooth edges without specific and periodic atomic structures, and SWNTs cannot be aligned along the artificial steps. However, here we demonstrate that the nanotubes can be aligned on the trenches when appropriate etching technique and controlled nanotube synthesis are applied. With our current RIE setup, we have produced an average density of $\sim 1-2$ SWNTs $\mu$m$^{-1}$ of aligned nanotubes. It is, however, expected that such density as well as the alignment can be improved by making denser and perpendicular trenches. The creation of trench patterns for SWNTs alignment control makes our technique attractive for SWNT-based electronics that can be reproduced for mass production.

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