Kyushu University Global COE Program
Journal of Novel Carbon Resource Sciences, Vol. 2, pp. 36-40, Sep. 2010

Micro Review

Methods to Horizontally Align Single-Walled Carbon Nanotubes on Amorphous Substrate

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(Received July 9, 2010; accepted August 20, 2010)

Synthesis of horizontally-aligned single-walled carbon nanotube on amorphous silicon dioxide is an important goal for direct integration of carbon nanotubes into the current modern nanoelectronics. In this micro review, we will overview the methods done to achieve a horizontally aligned single-walled carbon nanotubes on amorphous SiO_2 as well as present our recent works in which we modify the substrate to guide the nanotubes during growth. In addition, we present our nanotube-based field-effect transistor that was created using the aligned nanotubes directly grown on silicon substrate.

1. Introduction

Single-walled carbon nanotube (SWNT), a highly crystalline 1D nanomaterial made of carbon atoms and just a few nanometer in diameter, has been of interest for more than a decade due its superior mechanical, optical, and electrical properties[1)]. One remarkable property of SWNTs suitable for nanoelectronics is the extraordinary high field-effect mobilities of up to several 10,000 $cm^2 V^{-1}s^{-1}$ [2)]. However, for SWNTs to be integrated in nanoelectronics, the capability to control both position and direction is imperative since the current silicon-based electronics are fabricated in a highly ordered geometry. This horizontal alignment on suitable substrates remains to be one of the fundamental issues for nanotube-based electronics. Furthermore, position control and horizontal alignment of SWNTs on silicon (Si) with an oxide layer (SiO_2/Si) is most desirable since most of the electronic devices are based on single-crystal silicon wafers[3)].

Horizontal alignment of SWNTs on single crystals such as sapphire (α-Al_2O_3) and quartz (SiO_2) substrates have already been observed and experimented. The proposed mechanism is that SWNTs follow a particular atomic arrangement[4-7)] or along the ordered atomic steps after substrate treatment[8,9)]. Thus, due to the homogeneity of the atomic arrangement or atomic steps, the aligned nanotubes are very straight and distinct from each other. Such results are important for future nanoelectronics applications since the self-assembled horizontal alignment of SWNTs conveniently solves the possible problem of inter-tube junctions that can greatly affect the overall network performance[10)].

On the other hand, SWNTs grown on SiO_2/Si substrate are random and overlap each other[11,12)]. Such growth behavior was attributed to the amorphous nature of SiO_2 where no directional force is available to guide the nanotubes. This problem can be solved by creating pre-fabricated surface structures which will be discussed in the later section.

As a result of this random growth on SiO_2/Si substrate, a transfer process from the aligned SWNT on single crystals has been developed to create a SWNT-based electronic device[13,14)]. To realize this, several groups have used an intermediate polymer which also acts as a rigid support to detach the weakly coupled SWNTs from the crystal substrate and mechanically transfer to the desired substrate. Consequently, the method possesses an intrinsic possibility for carbon nanotube contamination and deterioration and is often tedious[13,14)]. Also, such process is not ideal for large-scale carbon nanotube-based nanoelectronics applications. Therefore, it is highly desirable to directly grow dense and aligned carbon nanotubes on silicon.

Table 1 is a summary of the characteristics of the aligned carbon nanotubes on crystals and SiO_2/Si substrate. The realization of the desirable characteristics, which is shaded in yellow, is the primary objective of our group. For the past years, we have made considerable progress on the realization of dense, aligned, and self-organized growth of SWNTs on silicon substrate.

This micro review is aimed to present our recent results as well as the previous works done to align SWNTs

Table 1 Characteristics of the aligned SWNTs on two different substrates

	Crystal Substrates	***Amorphous SiO_2/Si***
Substrate Profile	crystalline, can form atomic steps[8,9)]	amorphous, cannot form atomic steps
SWNT Density	>50 SWNTs/μm[8)]	~3-8 SWNTs/μm[21)]
Growth Controllability	self-organized, aligned[4-9)]	random,[11,12)] needs external forces for alignment[15,16,19,20)]
Applicability to current FET configuration	Indirect, expensive	Direct, cheaper

on SiO_2/Si. Furthermore, we will introduce the two general methods in aligning SWNTs on the amorphous SiO_2/Si substrate; forced alignment and self-organized alignment. Though our group mainly focuses on self-organized alignment which was developed just recently, a background on the early attempts to align SWNTs on SiO_2/Si will also be presented. Lastly, we will also present the results on our fabricated field-effect transistors based from these aligned SWNTs.

2. Alignment by External Forces

2.1 Electric-Field Assisted Alignment

Since assembling SWNTs into organized structures is a pre-requisite for integration into the current electronic devices, it is imperative that a suitable method is established to realize this goal. One of the early attempts to align SWNTs directly on amorphous substrates is the use of electric field. The dependence of SWNTs under strong electric fields was first exploited by Dai and his colleague to align SWNTs on SiO_2/Si[15,16]. In their method, two metal electrodes were carefully assembled opposite with each other on top of the substrate. The electrodes were electrically wired outside the furnace to provide *in situ* electrical feedthroughs during SWNT chemical vapor deposition (CVD) growth. On top of the metal electrodes, the catalyst was patterned either via photolithography or by contact printing. Figure 1a shows the schematic diagram of the set-up used for electric field-assisted SWNT growth. Successful alignment was carried out after supplying optimized voltages during CVD growth. In this configuration, the electric field lines obtained through calculation are directed upwards near the catalyst strips where the nanotubes are grown[16]. It was then suggested that in order to align SWNT on SiO_2/Si substrate, a suitable electric field distribution must be applied to prevent the SWNT from binding via van der Waals force with the substrate surface. Their results also suggested that on the early stages of growth, the SWNTs "rise-up" from the catalyst surface and then follow the electric field line as they lengthen up. Based from this concept, a new concept not requiring an special set-up was developed – the gas flow induced alignment.

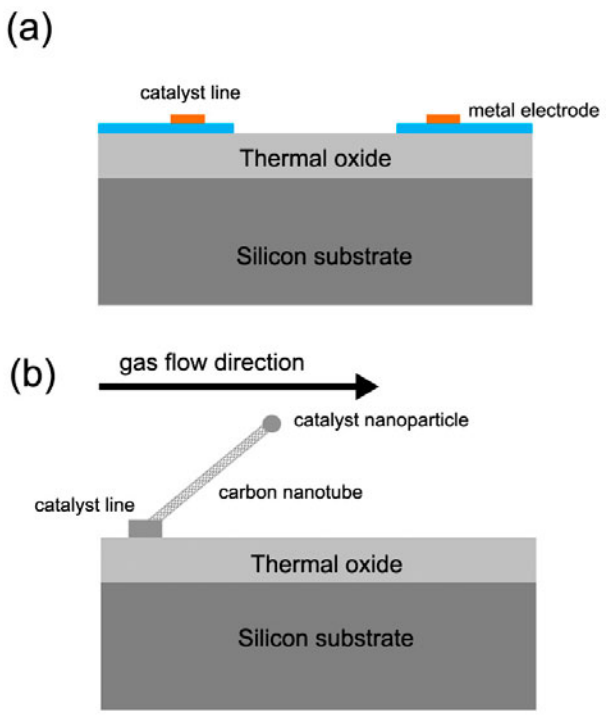

Fig. 1 Forced-alignment methods to align SWNTs on SiO_2/Si. (a) Cross-section view of the set-up used by Ural et al. for electric-field assisted alignment[16]. (b) Artist sketch to explain the mechanism of gas-flow assisted growth employed by Huang et al.[20]. This figure is adapted from literature.

2.2 Gas-Flow Induced Alignment

The introduction of electric-field to align SWNT proves to be tedious task considering it requires a special set-up. Also, the length and the density of the aligned SWNTs do not warrant scalability and practical applications. Longer and denser carbon nanotubes are needed for varied applications. For instance, ultra-long nanotubes can be made into fibers and integrated into materials improving its structural properties for high-strength and lightweight applications[17]. Also, multichannel devices made up of dense arrays of carbon nanotubes give out higher current outputs and promising on/off ratio[18]. With the advancing understanding on the growth of SWNTs, it was assumed that in order to synthesize long and aligned carbon nanotubes, SWNT-substrate interaction must be avoided. Additionally, catalytic thermal CVD proves to be the more practical method to obtain denser nanotubes. Thus, much effort has been allocated to modify CVD set-ups to prevent nanotube to substrate interactions during CVD. Liu's group was one of the pioneers to first obtain a long (mm scale) aligned growth of SWNTs[19,20]. They used a 2-furnace system designed to provide a "fast-heating" atmosphere of the sample at the initial stage of the growth. In this method, the Si wafer with the catalyst was transferred into the center of the furnace by either transferring the whole quartz tube containing the sample or by moving the furnace in the opposite direction so that the sample is relocated at the center of the heating zone. The concept was that on the initial stages of growth, the nanoparticle located at the tip of the carbon nanotube (tip-growth), avoids contact with the substrate by "lifting-up" from the surface as it grows longer (also-called the "kite-flying" mechanism)[20]. Figure 1b shows the artist sketch of the mechanism. As a consequence to the "lift-up" stage, the "fast-heating" CVD process was able to produce long carbon nanotubes in mm scale since no frictional force from the substrate is present to counter the growth. Another consequence to this condition is that the orientation of the long carbon nanotubes was determined by the gas flow direction. This "gas-flow" assisted alignment provides a more realistic set-up for growing long and aligned single-walled carbon nanotubes. One drawback with this method is that the density of aligned nanotubes is very low (<0.5 SWNTs/μm)[19,20].

3. Alignment by Substrate Modification

Single crystal substrates have been found to show atomic steps when annealed. These atomic steps were able to guide SWNTs aligning along the steps[8,9]. This proves that surfaces of substrates can affect the orientation of the nanotubes. Recently, a systematic study on the effect of surface morphology of silicon on SWNTs alignment reveals that on the onset of SWNT growth, the SWNT are random and needs a particular length (3 μm in their studies) for alignment to occur[21]. This length-dependent alignment on SiO_2/Si supports the earlier alignment study conducted by other group[22]. We have taken this concept by making artificial steps on SiO_2/Si wafer[23,24,26]. We have treated the Si wafer with CF_4 plasma to artificially create trenches on SiO_2. After treatment, random radial trenches were created on SiO_2 with depth of ~ 5 nm[23]. Shown in Figure 2a is an atomic force microscope (AFM) image on one of the created trenches. Afterwards, normal CVD growth was performed on these wafers. It should be noted that no special set-up was used in this experiment. Shown in Figure 2b is the result after CVD growth. It was found that SWNTs are aligned radially along the created steps. Though the grown carbon nanotubes are dense (3-8 SWNTs/μm), their position within the wafer is uncontrollable.

We have further developed these findings by systematically making artificial trenches with widths between 100-500 nm via electron beam (EB) lithography and reactive ion etching (RIE)[24]. In this way, we can create a more defined and controllable position of the trenches for SWNT alignment. The depths of the trenches can be controlled by controlling the etching parameters of the RIE. Shown in Figure 2c is the scanning electron microscope (SEM) image of the trench profile. Inset is the cross-sectional SEM image of the trenches after tilting the substrate. The catalyst was then patterned perpendicular to the trench direction to investigate the influence of the trenches to the growth of the SWNTs. After CVD, SWNTs aligned along the trenches as shown in Figure 2d. Interestingly, the carbon nanotubes aligned along the trenches regardless of the gas flow direction (shown in the arrow of Fig 2d). This clearly shows that the alignment was influenced by the trenches. We have inferred that the alignment was due to the SWNTs being captured at the edge and bottom of the trench. The mechanism is that during growth, the nanotube was "caught" at the edge of the trench (indicated by position 1 of Fig 2e) was able to "escape" and get "caught" again (indicated by position 2 of Fig 2e). Inset of Figure 2e is a schematic illustration of the carbon nanotube being captured at the corners of the created trench in Figure 2e. It is worth noting that the shape of the RIE-etched trenches (U-shaped) as shown in the inset of Fig 2c do not consistently give perpendicular surfaces so that the nanotubes can escape from the trenches and can sometimes glide over the trench. Due to this "caught-escape-caught" mechanism, the alignment is not as high as compared to single crystals. The same mechanism was also proposed by other group (it was termed "stick at first") though they also suggested a "rise-up" mechanism[25]. Shown in Figure 2f is the radial breathing (RBM) mode of the aligned carbon nanotubes which determines that the aligned carbon nanotubes are single-walled. From the formula $d = 248/\omega_{RBM}$, where d and ω_{RBM} are diameter and RBM frequency, respectively, the diameter was estimated to be 1.2 nm.

Since the results suggested that the trench structure is essential for improving the degree of SWNT alignment, a new trench structure was experimented[26]. Anisotropic

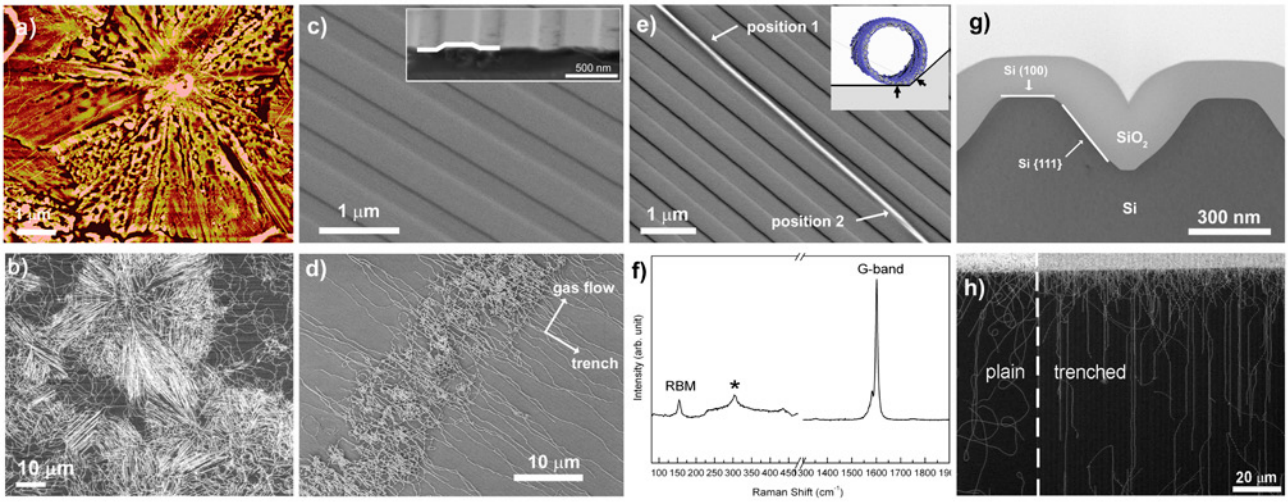

Fig. 2 Self-organized methods to align SWNTs on SiO_2/Si. (a) AFM image of SiO_2/Si substrate after CF_4 etching and (b) the corresponding SEM image after CVD nanotube growth. (c) SEM image of the trench on SiO_2 created after EB lithography and RIE (Inset is the SEM image of the tilted substrate) and (d) the SEM image after nanotube growth. (e) SEM image of the captured nanotube on the trench (Inset is the schematic image, see text for details) and (f) the representative Raman data of the captured nanotube. (g) STEM cross-section image of the trench profile made using anisotropic etching with the indicated crystal surfaces. (h) SEM image of the nanotubes after CVD growth. This figure is adapted from Yoshihara et al.[23] and Orofeo et al.[24,26].

etching of Si wafers was employed to create V-shaped trenches. This kind of trench and method is expected to create a more defined structure in terms of shape since it uses the orientation-dependent etching of Si against some etchants. It is known that Si(100) surface etches 100 times faster than Si(111) in potassium hydroxide(KOH) solution. With proper mask orientation, a precise V-shaped groove can be formed with Si{111} surfaces making an angle of 54.7° with respect to Si(100). Shown in Figure 2g is the scanning transmission electron microscope (STEM) image of the trench profile created on the Si. Indicated are the different crystallographic planes of Si. The SiO_2 layer, which was grown after anisotropic etching, retains the V-shape form of Si and has a smooth and sharp bottom edge. The SEM image of the aligned nanotubes on the trench and plain silicon after CVD was shown in Figure 2h. It can be seen that on the trenched part (right-side of the border), the nanotubes were straight and distinct from each other while on the plain part (left-side of the border), the nanotubes were randomly oriented. This result clearly shows that the trench pattern determines the direction of the nanotubes growth. Further investigation has led us to conclude that on the early part of nanotube growth, the trenches prevents the nanotubes from sliding randomly across the surface and aligns along the trenches as it grows. The method presented a solution to the random sliding of carbon nanotubes during growth presented by earlier studies. However, the relatively wide interspacing (~700 nm) between trenches cannot compete with the density of the aligned nanotubes on single crystal substrates. Nonetheless, the density of the aligned nanotubes is higher than the previously reported aligned nanotubes on silicon substrates[19,20]. The increase in density and alignment was attributed to the combined "trench-assisted" alignment together with the gas-flow assisted alignment described earlier. The degree of alignment is even comparable to the preliminary works of aligned carbon nanotubes on stepped crystal substrates[9]. These results are expected to provide new insights on carbon nanotubes' alignment on SiO_2/Si and offer an alternative to the possibility of large-scale integrated SWNT electronics for mass production.

4. Field-Effect Transistor (FET) Fabrication

Since we have grown SWNTs directly on SiO_2/Si, we can readily create FET with the aligned SWNTs by evaporating gold electrodes that will serve as source and drain contacts and with the silicon serving as the gate contact as shown in Figure 3(left). Measurement of the created device showed a well-behaved semiconducting behavior after breakdown of metallic nanotubes (Fig 3, right). We have measured more than 10 devices and the on/off ratio ranges from 10 to 10^4 with an average value of 10^3 [24], comparable to other studies involving SWNTs on silicon substrate[27]. The device mobility was computed to be ~ 5 $cm^2\ V^{-1}s^{-1}$ which is much higher than the typical organic transistor of 0.1 $cm^2\ V^{-1}s^{-1}$ [28]. Results showed promising FET characteristics that proves SWNTs' capability as future material for nanoelectronics.

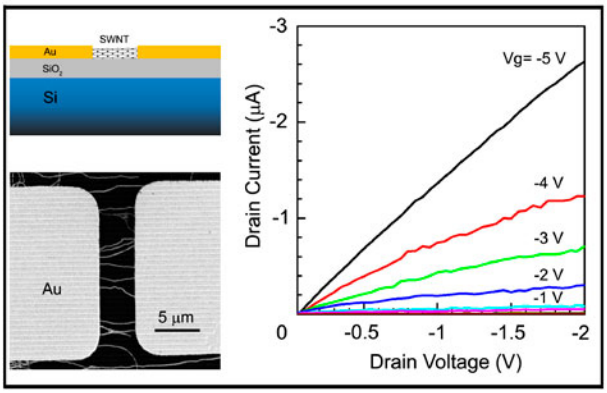

Fig. 3 Carbon-nanotube based field-effect transistor. (Left) Configuration of the FET using SWNTs, (Right) I_d-V_d curve of the device after breakdown of metallic SWNTs. V_g are indicated with step of 1 V.

5. Conclusions

We present the methods of horizontally aligning SWNTs on amorphous silicon substrate. Two general methods were presented, the forced-alignment methods wherein external forces were used to align the nanotubes and the self-organized alignment method where the silicon substrate was modified for alignment. Although both methods are still inferior compared to alignment on crystals in terms of both density and degree of alignment, it is still a step further for the realization of SWNT-based nanoelectronics.

The creation of artificial trenches on SiO_2 provides a wider avenue for improvement in terms of attaining highly dense and aligned SWNTs desirable for mass production. The EB patterning proves to be the major bottleneck for large area patterning since the process itself is limited in terms of space and it is time-consuming. Nanoimprint lithography (NIL) can be utilized to pattern such structures with which the area is only limited to the size of the mold (Figure 4). The design of the mold can also be made finer since density of aligned nanotubes is expected to increase with denser trenches.

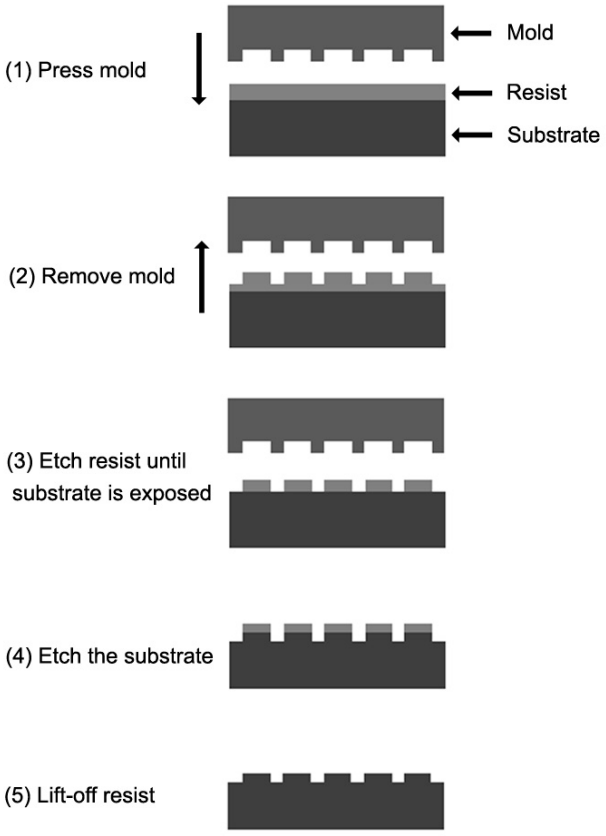

Fig. 4 Scheme of NIL for large area patterning of the trenches.

Acknowledgement: This study was supported by Grant-in-Aid for Scientific Research (21310074) of Ministry of Education, Culture, Sports, Science and Technology. CMO acknowledges the GCOE for partially funding the research.

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