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Thermally enhanced single-walled carbon nanotube microfluidic alignment

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ABSTRACT

We present thermally enhanced single-walled carbon nanotube (SWCNT) horizontal alignment on a wafer scale level that enhances the device performance with a possibility of mass production. The SWCNT dispersion is evaporated on the heated and tilted open microfluidic channel template of photoresist. Scanning electron microscopy demonstrates well-aligned SWCNTs qualitatively and G-band to D-band (G/D) ratio in Raman spectra indicates the degree of alignment quantitatively. The effect of temperature, fluidic channel dimension, concentration of SWCNT dispersion and wetting properties on the alignment is investigated, resulting in G/D ratio of up to 30.

1. Introduction

The carbon nanotube (CNT) has been used for a variety of applications such as transistors [1,2], sensors [3,4], actuators [5], and solar cells [6] due to its remarkable mechanical, electrical, optical and electrochemical properties. The selective placement and controlled alignment over a large area are required for assembled CNTs to be fully functional on matrix devices. The alignment of CNTs is essential to enhance the device performance [7], adjust the mechanical and electrical properties [8], and tune material anisotropicity. Particularly, the post-growth assembly and alignment are of much interest considering CNTs as the off-the-shelf raw building blocks aiming at nanoengineered structures. The *in situ* growth alignment such as chemical vapor deposition (CVD) with an external force was optimized for the vertical alignment and attained a high density and perfect alignment [9], which was offset by a high synthesis temperature. The horizontal alignments of CNTs have been accomplished through chemical vapor deposition (CVD) [7], dielectrophoresis [10,11], dip-coating [12], fluidic flow [13,14] and spin-coat [2]. Although CVD achieved good alignment whose G-band to D-band (G/D) ratio of more than 20 was demonstrated in Raman spectra, it did not make dense and uniform film [15]. Furthermore, the alignment schemes that used the external fields lack the large area capability. We addressed these issues with a scalable thermally enhanced SWCNT alignment using open microfluidic channels prepared by lithographic techniques.

2. Experimental section

The thermally enhanced microfluidic alignment scheme we adopted was performed as follows. The photoresist microfluidic channel was fabricated by photolithography on a silicon (Si) wafer with a 500 nm thick thermal oxide (SiO_2). Oxygen (O_2) plasma was applied at a power of 100 W and O_2 flow rate of 100 sccm for 1 min to change the wetting properties of the microfluidic channel template. At this moment, the photoresist channel template became super-hydrophilic while the wetting property of SiO_2 surface remained relatively hydrophobic. Subsequently, the template was dipped into Microposit 351 developer solution for 10 s. Finally, photoresist surface was transformed to hydrophobic whereas SiO_2 surface became hydrophilic. The substrate was put into SWCNT dispersion (PureTubes™, Nanointergris Inc., 0.25 wt.%) with a tilting angle of about 20° in the oven heated to the desired temperature as illustrated in Fig. 1(a). At this moment, the fluidic channel bottom was hydrophilic while the channel wall was hydrophobic. The microfluidic channel used was 2, 5, and 10 μm in width possessing a pitch of 2, 3, and 4 times of channel width. As-received SWCNT dispersion was diluted to produce 0.188 and 0.125 wt.% concentration followed by ultra-sonication for an hour. The oven temperatures used were 20–95 °C with 15 °C step. Surface profiler and atomic force microscopy (AFM) were used to measure the thickness of aligned SWCNT film. Furthermore, scanning electron microscopy (SEM) and Raman spectroscopy were employed to characterize the degree of alignment. The conditions for Raman spectroscopy were a wavelength of 514.5 nm and a power of 5 mW for 5 s.

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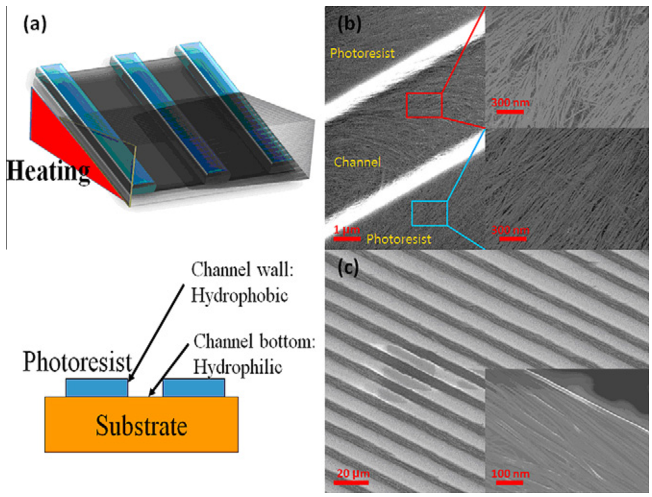

Fig. 1. The thermally enhanced microfluidic carbon nanotube alignment scheme: (a) a schematic of experimental setup, (b) scanning electron microscopy images of the aligned SWCNTs in the channel (right top) and on the photoresist (right bottom) before photoresist strip, and (c) scanning electron microscopy images of the aligned SWCNTs in the channel after photoresist strip: The alignment was performed with a channel width of 5 μm, the evaporation temperature of 60 °C and SWCNT concentration of 0.25 wt.%.

3. Results and discussion

Jung et al. [12] argued that the wetting property of the channels was important to enhance the alignment. They used gas plasma to treat the microfluidic template, avoiding the use of wet chemistry. However, herein, we used a simple lithographic approach to get an appropriate wetting property with an O_2 plasma treatments followed by a further develop. As a result of O_2 plasma etching followed by develop, hydrophobic channel wall and hydrophilic channel bottom were obtained. The SWCNT solution was evaporated gradually to leave the aligned SWCNTs all over the template surface. A good alignment was achieved not only in the channel but also on top of the photoresist fluidic channel as shown in Fig. 1(b). However, some of unaligned SWCNTs are observed in the channel (right top). The aligned SWCNT film in the fluidic channel is a primary concern in order to utilize it as a functional film after patterning. As the evaporation of SWCNT dispersant goes, the 3-phase line sweeps downstream, which leaves the aligned SWCNTs on the fluidic template. Then, lift-off was done to get the aligned SWCNTs in the fluidic channel with the aid of ultrasonication. In this process, the unaligned SWCNTs left in the channel were removed, leaving the well aligned tubes as shown in Fig. 1(c) presumably due to the interaction between CNTs and the substrate [2].

The microfluidic channels with different widths and pitches were fabricated on a 4 in. silicon wafer as shown in Fig. 2 to demonstrate wafer scale application. As the SWCNTs solution concentration changed with the deposition process going on, the film has varied thickness from one end of the wafer to the other. However, the film thickness was equated by one more time of deposition by rotating the wafer 180°. The wafer was soaked again into SWCNT dispersion and left for the 3-phase line to sweep the microfluidic channel in the other direction. Fig. 2(b) shows the aligned SWCNT thin film in the channel with 5 μm width and 20 μm pitch. The thickness of aligned SWCNT film was measured across the lengthwise by surface profiler. The surface profile in Fig. 2(c) was measured across the length in the middle of downstream pattern in Fig. 2(a). Actually, several measurements were performed both downstream and upstream patterns and resultant profiles were found to be similar.

The Raman spectroscopy has been used for the characterization of the purity and alignment of CNTs synthesized [16,17]. In this work, the G-band was forced to have the same values at each acquisition of spectrum, so that the G-band (graphitic-like) to D-band (disorder-induced) intensity ratio can be used to quantify the degree of alignment [18]. The effects of evaporation temperature and fluidic channel width on the alignment with 0.25 wt.% concentration are shown in Fig. 3. A high degree of alignment was found in 10, 5, and 2 μm wide channels prepared at a temperature of 80 °C as shown in Fig. 3(a)–(c). Furthermore, the

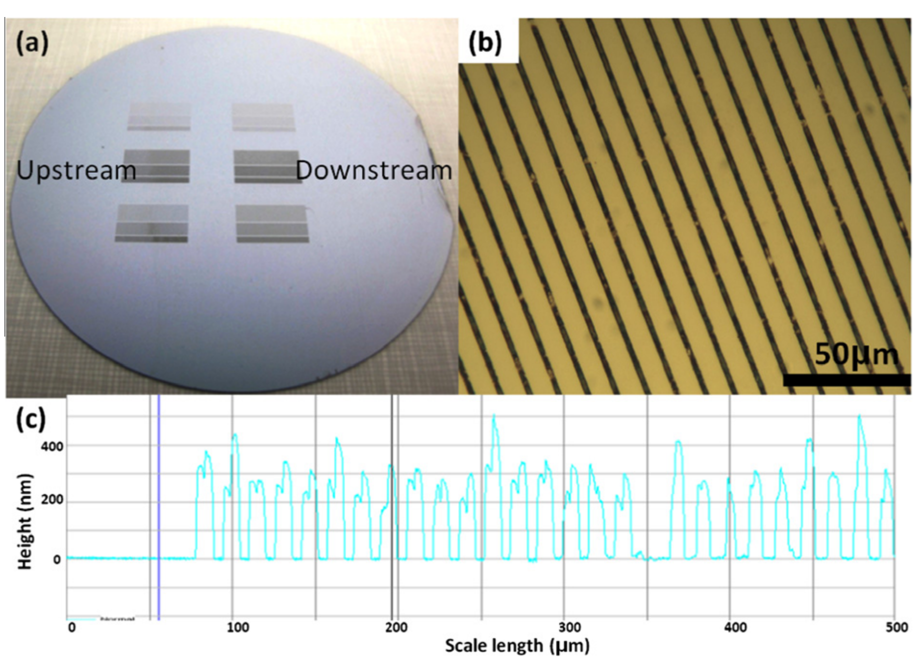

Fig. 2. SWCNT alignment at 4 in. wafer scale level: (a) optical image of SWCNT deposited on a 4 in. wafer with different channel widths and pitches, (b) optical microscope image of SWCNT patterns from upstream after stripping photoresist, and (c) surface profile of patterned SWCNT patterns in (b) that was extracted from the middle of downstream pattern in (a).

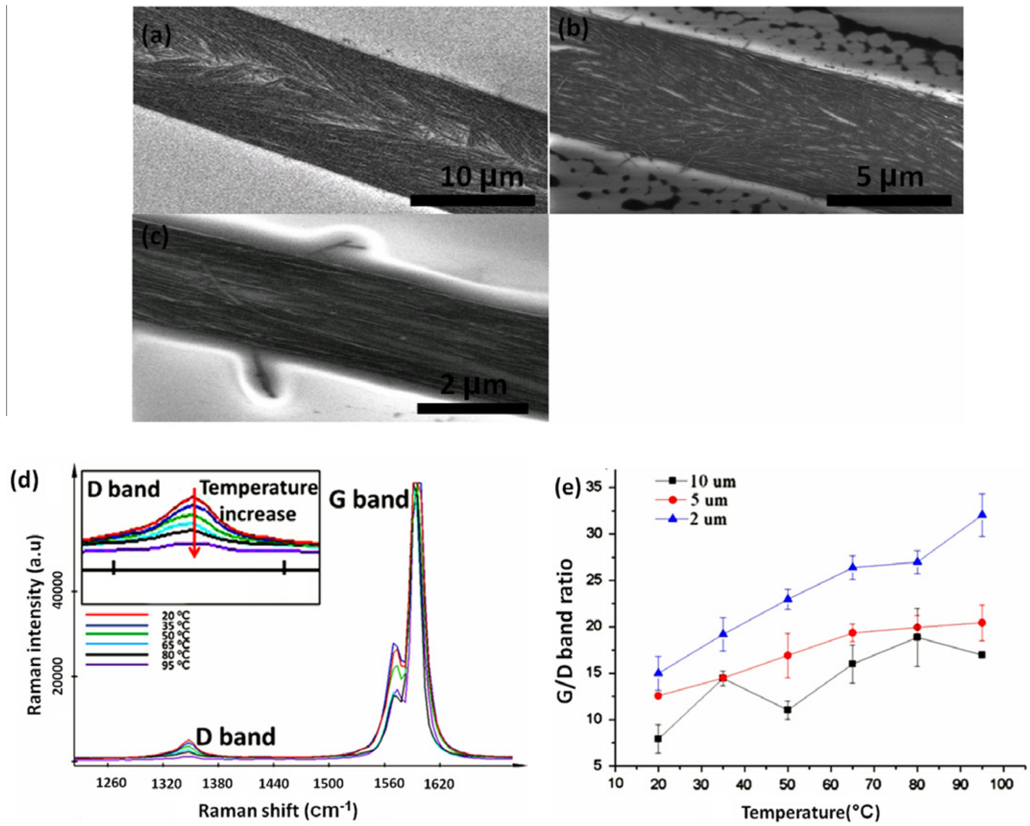

Fig. 3. The effects of evaporation temperature and fluidic channel width on the alignment with 0.25 wt.% SWCNT concentration: (a–c) SEM images of aligned SWCNTs in 10, 5, and 2 μm wide channel made at 80 °C, (d) Raman spectra of samples aligned at different temperatures in 5 μm wide channel, (e) comparison of G/D band ratios.

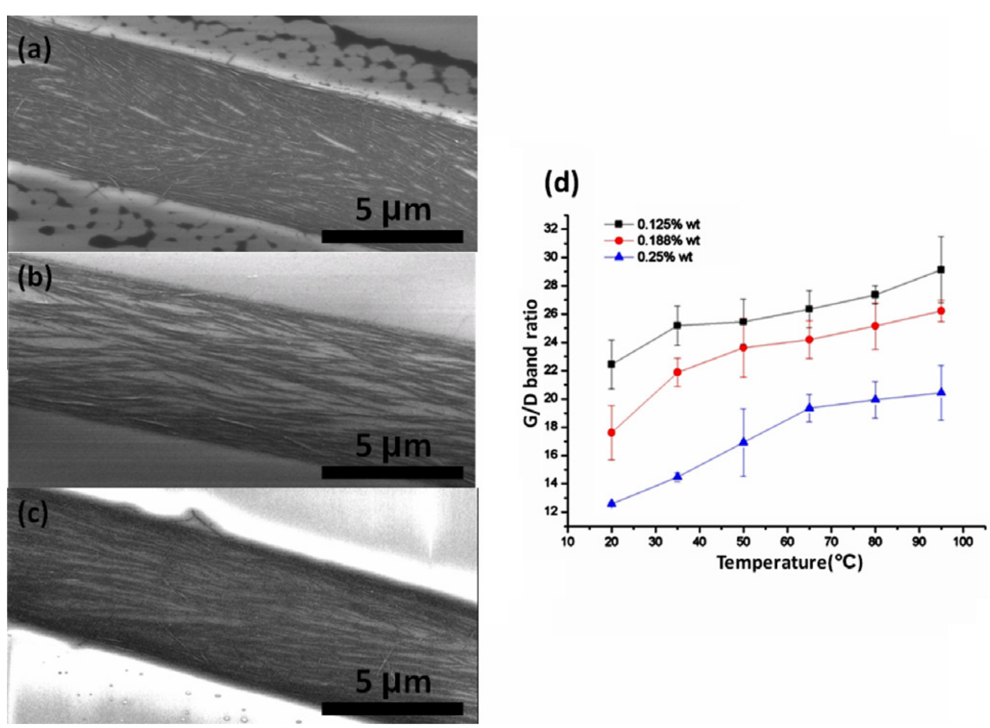

Fig. 4. The effect of the SWCNT concentration on the alignment: (a–c) SEM images of the aligned SWCNTs with 0.25, 0.188 and 0.125 wt.% concentration in 5 μm wide channel at 80 °C, and (d) G/D band ratio of aligned SWCNTs under different temperatures.

confinement effect becomes significant as the channel width decreases, so that the degree of alignment augments. The evaporation temperature also plays an important role in the fluidic alignment. At different temperatures from 20 to 95 °C in constant 5 μm

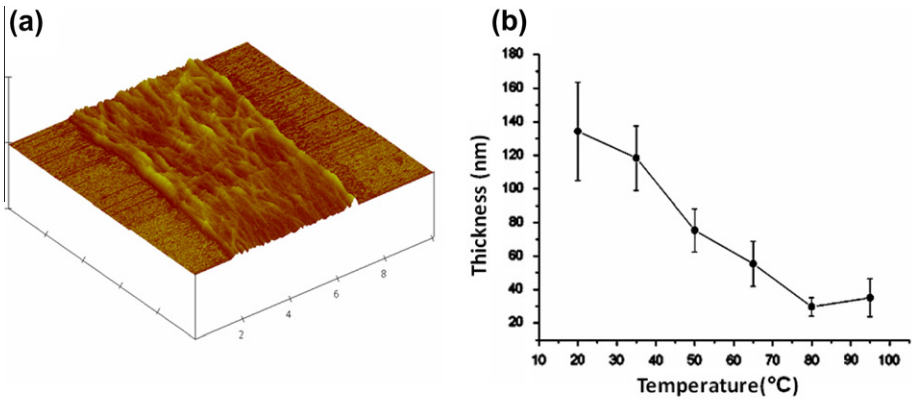

Fig. 5. Surface profile characterization: (a) atomic force microscope (AFM) image of the aligned film at 80 °C in 5 μm wide channel, and (b) thickness of aligned films made in 5 μm wide channel under different temperature.

channel width with 0.25 wt.% SWCNT concentration, Raman spectra were collected, as shown in Fig. 3(d), where the G ($\sim$1590 cm^{-1})/D ($\sim$1350 cm^{-1}) band ratio was calculated as an indication of quantitative degree of alignment. As shown in Fig. 3(e), G/D band ratio increases with an increase of temperature. It is obvious that a higher G/D band ratio was obtained for the 2 μm sample than 5 and 10 μm samples presumably due to the enhanced confinement. The maximum G/D band ratio of up to 30 was found in the 2 μm samples heated at 95 °C. To the best of our knowledge, this is the highest value ever reported [18,19].

The degree of alignment is also affected by the concentration of the SWCNT solution. Under the constant evaporation temperature at 80 °C and channel width of 5 μm, as shown in Fig. 4(a)–(c), the degree of alignment increases as the concentration of the SWCNTs solution decreases. The G/D band ratio in Raman spectra indicates that better alignment is achieved at lower concentration as well as at higher evaporation temperature as shown in Fig. 4(d). However, less SWCNTs are observed in the samples prepared with 0.125 wt.% than 0.25 wt.% concentration. It seems that the interaction between SWCNTs and substrate plays an important role in the alignment of CNTs [20]. One end of SWCNTs is attached onto the substrate and flow-induced shear stress makes the alignment along the flow direction. However, the interaction among SWCNTs in a high SWCNT concentration becomes more dominant than the tube-substrate interaction, so that it might hamper the flow-induced aligning process. Furthermore, as the number of SWCNTs participating in aligning process increases, the interaction among those SWCNTs comes into play, resulting in graphitic mismatches among tubes.

In addition, the temperature has an effect on the SWCNT film thickness. Since sweeping velocity of 3-phase line over the microfluidic template depends on the evaporation rate that was influenced by temperature. Therefore, the residence time of SWCNTs at specific position of the channel is inversely proportional to

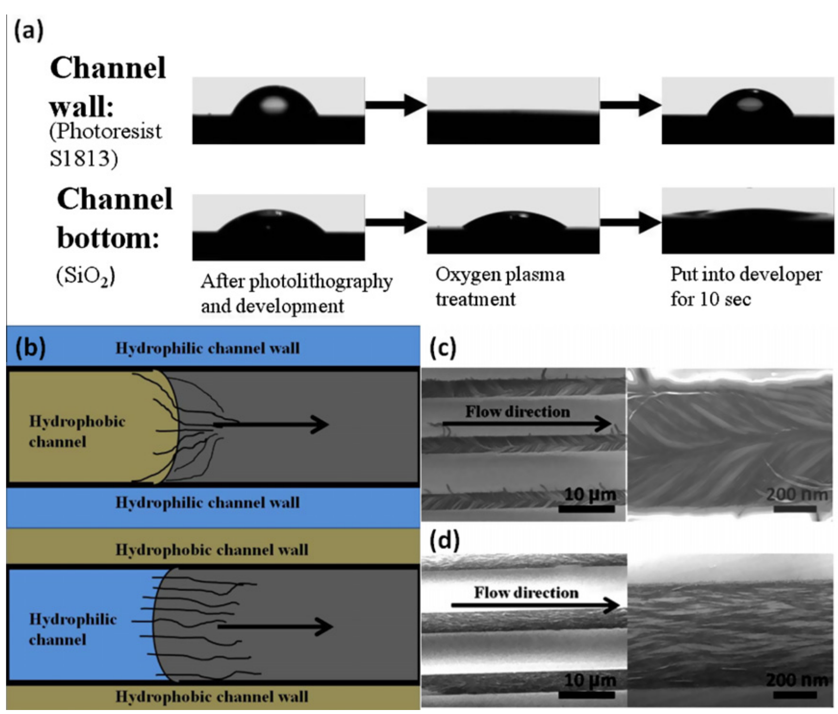

Fig. 6. The effect of wetting properties on the alignment: (a) the contact angle measurement of the sample surface, (b) the scheme of the alignment on the substrate with different wetting properties, SEM images of aligned SWCNTs (c) on the hydrophobic channel bottom and the hydrophilic wall, and (d) on the hydrophilic channel bottom with the hydrophilic wall.

sweeping velocity of 3-phase line. Therefore, the evaporation is slow at lower temperatures, allowing more time for SWCNTs to be assembled, which leaves more SWCNTs on the unit area. Thickness of aligned film was measured using AFM as shown in Fig. 5(a), which was taken from the sample made in 5 μm wide channel at 80 °C. The thickness of the aligned film decreases as the temperature increases, as shown in Fig. 5(b). However, more study on modeling of the interaction of gas–liquid–solid interface with tubes in liquid is needed.

The wetting properties of the surface had significant influence on the SWCNT alignment. We fabricated two types of microfluidic templates with different wetting properties using the purely lithographic approach: one with hydrophobic channel bottom and hydrophilic channel wall and the other with hydrophilic channel bottom and hydrophobic channel wall. The former template was obtained after O_2 plasma treatment, and the latter was accomplished by re-development as shown in Fig. 6(a), where the static water contact angle measurements at each step of microfluidic channel preparation are depicted. The different orientation of aligned SWCNTs film is expected due to the different wetting properties. The different wetting properties of the channel bottom and channel wall result in different shear stress as liquid flow passes by [21], which affects the alignment of SWCNTs. When the liquid flow passes by the hydrophilic surface, compared to that of hydrophobic surface, there is larger shear stress generated in the boundary layer. Larger shear stress leads to greater resistance to the flow. For the channel with hydrophilic wall and hydrophobic bottom, there is large shear stress near the channel walls and small shear stress near the channel bottom. The stress field distribution results in the orientation of the SWCNTs as shown in Fig. 6(c). For the channel with hydrophobic wall and hydrophilic bottom, there is small shear stress near the channel walls and large shear stress near the channel bottom, however because the effects of the boundary layer, the flow in the channel has a relative uniform velocity profile along the cross section which results in the orientation of the SWCNTs as shown in Fig. 6(d).

4. Conclusion

In conclusion, we present a thermally enhanced fluidic alignment of SWCNTs on 4 in. wafers, which resulted in the outstanding degree of alignment in large scale. This work is featured by the facile lithographic process, which has a potential for mass production of CNT-based devices. It resulted in a good degree of alignment with a G/D band ratio up to 30, which is the highest ever reported. The evaporation temperature, microfluidic channel dimension, concentration of SWCNT dispersion, and wetting properties of the template influence the alignment. Temperature plays the most important role in controlling the degree of alignment. It has a variety of potential applications to enhance the performance of devices such as transistors, sensors, and actuators [5] since aligned thin film has better mechanical and electronic transporting properties than unaligned film.

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