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Temperature effect on the substrate selectivity of carbon nanotube growth in floating chemical vapor deposition

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Abstract
An easy approach to control the carbon nanotube (CNT) array selectivity on Si/SiO_2 in the floating chemical vapor deposition (CVD) method by adjusting the operation temperature is demonstrated. Aligned CNTs can be obtained directly on Si using a standard procedure at a relatively low temperature. After analyzing the temperature influence on different substrates, an attempt to grow an ultra-long CNT forest at the optimized temperature and without any feedstock diffusion limitation is discussed.

S Supplementary data are available from stacks.iop.org/Nano/18/415703

The superior electrical properties of a carbon nanotube (CNT), e.g. chirality-dependent conductivity, ballistic electron transport, super-high current-carrying capacity, and good field-emission performance, make it one of the most promising building blocks for future electronic devices [1–4]. In order to incorporate CNTs into current micro-electromechanical system/nano-electromechanical system (MEMS/NEMS) procedures, the effective and controllable growth of CNTs directly on specific substrates, especially silicon, is essential. Many methods have been proposed to first prepare available catalyst particles or films on a substrate and then grow CNTs in the form of macroscopic arrays on this through chemical vapor deposition (CVD) [3, 5–8]. However, the attractive ferrocene-based CVD [7, 9, 10] (also called spray pyrolysis, injection CVD and floating CVD) process, in which the whole CVD process is greatly simplified because no complicated catalyst pre-deposition is required, failed to yield dense CNT arrays on silicon directly. This was explained as being caused by the high activity between iron and silicon that resulted in the formation of inactive $FeSi_2$ or $FeSiO_4$ [11–14]. This view was challenged when Zhang [15] presented data that showed that CNT arrays can also be grown on silicon. However, this was only with the use of a much higher catalyst concentration and operation pressure. Also, there are numerous reports on the successful atmospheric pressure growth on silicon when 1–10 nm iron layers were sputtered or vapor deposited (i.e. thermal CVD) as the catalyst. One big difference between floating and thermal CVD is that the latter process is usually performed at relatively lower temperatures, e.g. from 700 to 750 °C. Taking this as a clue, we suspect that the temperature can be another critical or even more effective control parameter in growing CNT arrays on silicon in floating CVD. In this work, we demonstrate that the CNT selectivity in growth using ferrocene pyrolysis can be easily controlled by adjusting the operation temperature. Aligned CNT arrays were obtained on silicon with no oxide layer through a standard floating CVD procedure at a relatively low temperature. After analyzing the temperature influence on different substrates, an attempt to grow an ultra-long CNT forest at the optimized temperature and without any feedstock diffusion limitation on the same patterned substrate is also discussed.

The aligned CNT arrays were synthesized using ferrocene as the catalyst precursor and hexane as the carbon source in a quartz tube reactor (inner diameter 1 inch, length 1200 mm, heating zone 700 mm) with the growth substrates placed in the center of the quartz tube, in an arrangement similar to that in our previous works [16, 17]. The first substrate, a 50 nm thick

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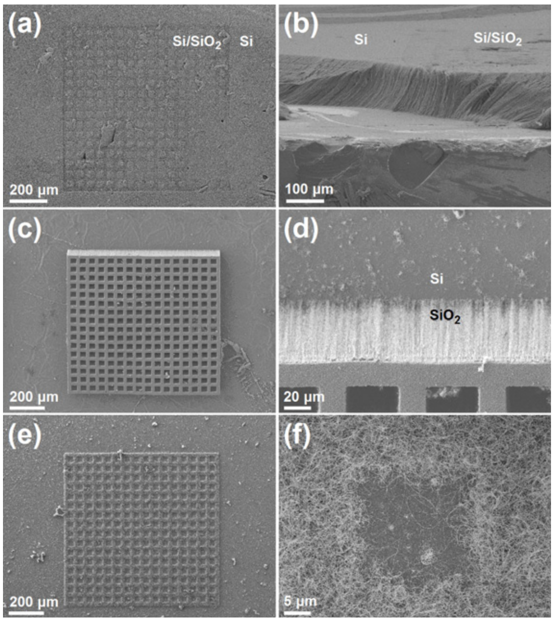

Figure 1. Morphologies of the as-grown carbon nanotubes patterned on a silicon oxide or silicon substrate at different temperatures: (a), (b) 710 °C, (c), (d) 780 °C, (e), (f) 820 °C, showing that the substrate selectivity can be easily controlled by the temperature. Aligned CNTs can be formed on silicon at a proper temperature. Images (a) and (b) are the top and cross-sectional views of the same sample. Images (c)–(f) were obtained with a tilt angle of 20°.

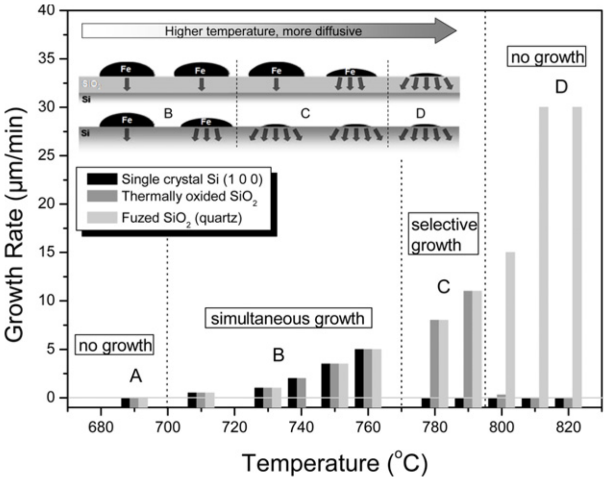

Figure 2. Detailed influence of the temperature on the growth rate of a CNT forest and its possible mechanism (top left inset): the whole operation range can be divided into four regions according to the different rates of CNT growth on Si and the thermal SiO$_2$ layer.

SiO$_2$ patterned Si(100) wafer, was fabricated by the thermal oxidation of Si in an oxygen and water atmosphere, and then the subsequent use of a standard photolithography wet etching procedure. The second substrate, a Pt patterned quartz used in the later part of this work, was obtained by first sputtering and then by the subsequent use of photolithography lift-off (the fabrication details are given in the supporting information available at stacks.iop.org/Nano/18/415703). Both substrates have a line width (SiO$_2$ region) of 20 μm and an inner square (Si or Pt region) size of 40 μm × 40 μm. A typical experiment was performed as follows. First, the furnace was heated to the desired temperature, from 690 to 820 °C, in an atmosphere of 600 sccm Ar (containing 10% H_2) as the carrier gas. Then a 20 mg ml^{-1} ferrocene and cyclohexane solution was injected at 9.6 ml h^{-1} through a syringe pump into the entrance of the heating zone, where the temperature was around 200 °C. The liquid feedstock evaporated and entered the reaction zone with the Ar/H_2 carrier gas and was deposited to form CNTs on the substrate. After a CVD time of 5–180 min, the feedstock injection was stopped and the furnace was cooled down to room temperature. The substrates with as-grown products were taken out and characterized by scanning electron microscopy (SEM; JEOL 7401F, excited at 3.0 kV).

Figure 1 shows the morphologies of the aligned CNT arrays grown at different temperatures on the same Si/SiO$_2$ patterned substrate. It clearly shows that, at a low temperature, e.g. 710 °C shown in figures 1(a) and (b), CNTs can grow on both Si and the thermal oxide SiO$_2$ using a standard CVD procedure. The CNTs grown on the Si region are of the same length as those grown on SiO$_2$. Here, we emphasize that we used a standard concentration (widely used in previous reports) ferrocene solution and atmospheric pressure, in contrast to the saturated solution and high pressure used by Zhang [15]. In our experiment, it was found that a higher concentration gave deteriorated CNT morphology and quality due to the rapid formation of large amounts of metal impurities and short but thick CNTs. With our current method, good morphology and high-quality CNTs can be maintained (see supporting material available at stacks.iop.org/Nano/18/415703). Meanwhile, the lower operation temperature and pressure are more controllable and cost effective. Compared to the method employing more roughness on the Si substrate (scratch, side wall, or implantation) [18–20], the current method is much easier, as no special substrate treatment is needed.

Figures 1(c) and (d) show the product when the reactor was at a little higher temperature, The CNTs only grew on the oxide region and thereby grew into predetermined patterns, which have been intensively studied [11, 13, 14]. Interestingly, when we further increased the growth temperature to 810 °C and higher, neither the Si nor 50 nm SiO$_2$ could support the growth of a dense and thick CNT mat, and there was uniform substrate inactivity, as shown in figures 1(e) and (f). Also, when the temperature was too low, that is, lower than 700 °C, no CNTs could be obtained (data not shown). As all the substrates used in the above experiments were from the same 2 inch Si wafer and the temperature was the only parameter changed, the temperature was responsible for this growth selectivity change. We have explored the temperature range from 690 to 820 °C and measured the average growth rate of the CNT arrays on Si, thermal oxide SiO$_2$ and quartz (the most widely used substrate). The operation temperature can be divided into four regions, which are identified in figure 2.

A previous explanation of the growth on the oxide layer clearly showed that, due to the high activity between Fe and Si, the catalyst lost its activity after the formation of FeSi$_2$ and FeSiO$_4$ [12]. The successful growth at a higher ferrocene concentration and operation pressure was explained as being that these provided excess metal species that form extra growth sites on top of the FeSi$_2$ and FeSiO$_4$ layer [15].

This means that the catalyst deposition on Si can be considered as a competition between catalyst formation and consumption (through the formation of $FeSi_2$ and $FeSiO_4$). When the catalyst consumption is lower than the formation, as when a higher ferrocene concentration is used, the excess metal catalyst can yield CNTs arrays. Here, in contrast, instead of doubling or tripling the catalyst precursor concentration and thereby sacrificing product quality, we have alternatively found a way to slow down the rapid reaction of iron with Si by the use of temperature control. Although the phase diagram of Si and Fe indicated a similar equilibrium structure and concentration up to 1100 °C, the time needed to reach equilibrium (due to the diffusion rate of iron atom into the Si lattice) is different at different temperatures [21]. Istratov reported that the iron diffusion coefficient in Si has a temperature dependence that can be expressed by the Arrhenius equation with an activation energy of 0.65 eV [22]. According to this, when the growth temperature is lowered by 50–100 °C, the iron diffusion rate is decreased by more than half. Then, the normal feeding rate of ferrocene is high enough to maintain a sufficient amount of catalyst for CNT growth on Si (region B). For a given feed rate of ferrocene, a higher temperature gives a faster consumption of iron until there is not enough catalyst, which finally hinders the effective formation of a thick CNT film. The SiO_2 layer can be understood as a buffer layer between iron and Si because iron diffusion in SiO_2 is more than ten orders of magnitude slower than in Si. When the oxide layer is present, the diffusion rate is slower, and thus selective growth on silicon and silicon oxide was obtained in this temperature range (region C). However, a 50 nm SiO_2 layer will still fail to protect iron from Si at even higher temperatures, and above 800 °C, neither Si nor SiO_2 can support effective CNT growth (region D). Although there were still some CNTs on the SiO_2 region at 820 °C, as shown in figure 1(f), the growth rate was negligible (<1 μm after 30 min growth) and the CNTs in the final film were too short to have good alignment. The temperature influence is illustrated in the top left inset of figure 2. Also, it is worth noting that these results (growth rates at different temperatures) were reproducible over several experiments. The growth rate decline always happened quickly within 10–20 °C on both Si and SiO_2. Further quantitative work is needed to fully understand the concentration change during this 10–20 °C.

The sustained and rapid growth of aligned CNT arrays on a patterned substrate, under conditions where the feedstock can reach the bottom of the forest growth points without diffusion limitation, is a useful strategy to obtain ultra-long CNT arrays, as demonstrated by Zhong [23]. However, the experiments to determine the operation temperature range shown in figure 2 indicated that the highest CNT growth rate was obtained around 810–820 °C (the grow rate decreased at temperatures higher than 820 °C), which is not in the selective growth region C. Therefore, Si/SiO_2 is not a good pattern substrate for growing CNTs with the highest efficiency (growth rate). Another possible route to assemble CNT arrays into patterns was introduced by Cao using Au as the growth shield [24]. Following the idea that Au will evaporate gradually at elevated temperatures as discussed by Zhang [15], we used Pt as the shielding material, and confirmed that it was effective, as shown in the following.

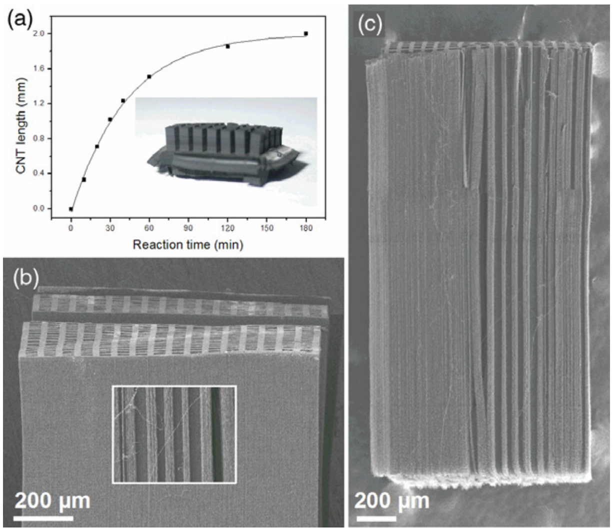

Figure 3. (a) Structure-independent decreased rate of growth of an aligned CNT forest in floating CVD that confirmed that this process was free of diffusion limitation, with the inset showing the as-grown CNT pillars on a Pt patterned quartz substrate; (b) enlarged SEM micrograph of the aligned CNT patterns, with the inset showing the inner hollow structure; (c) SEM micrograph of the continuous channels inside a single CNT pillar. The images of the inner channels were obtained after cutting one CNT pillar (0.98 mm × 0.98 mm × 2 mm) into two halves.

Figure 3(a) presents the time-dependent growth curve of our CNT arrays on a substrate with no patterns. The growth usually stopped after 1 h after growing to a little more than 2 mm. With the Pt/quartz substrate patterned as shown in the inset of figure 3(a), hollow CNT pillars were formed that still followed almost the same growth curve; that is, these also failed to grow continuously into longer arrays. We have previously proposed a simple dimensionless modulus $\varphi = k_s L/D_e$, where k_s is the reaction rate constant of the overall reaction from feedstock to CNTs, D_e is the feedstock diffusion coefficient inside the CNT film and L is the film thickness, to describe the difference between the tip and root feedstock concentration, i.e. the degree of diffusion limitation [25]. The results from this floating CVD process showed that there was nearly the same carbon source concentration at the CNT root as in the bulk gas phase. At that time, we were not sure if the catalyst precursor was also free of diffusion limitation because in that work we assumed that the diffusing species did not decompose until it reached the CNT root, which may be incorrect for the diffusion behavior of the metal precursor. Here, from this experiment, since the hollow channels inside of the arrays, as shown in figure 3(c), were not able to sustain the growth, we can conclude that neither the carbon source (cyclohexane) nor the catalyst precursor (ferrocene) diffusion limitation contributed to the decreasing growth rate in floating CVD. The reason for the growth deactivation needs further investigation.

In summary, it was demonstrated that the substrate selectivity of CNT growth from ferrocene-based floating CVD can be easily controlled by the operation temperature. At relatively lower temperatures, well-aligned CNT arrays can be grown directly on pure silicon even when this does not have an oxide top layer, obviating the need for a special substrate. A Pt patterned quartz substrate was used to grow hollow CNT pillars, and the observation that the final length of the CNT array was almost the same as that on the non-patterned substrate confirmed that there was neither carbon source nor catalyst precursor diffusion limitation in the growth process.

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References

[1] Wei B Q, Vajtai R and Ajayan P M 2001 *Appl. Phys. Lett.* **79** 1172
[2] Saito R, Dresselhaus G and Dresselhaus M S 1998 *Physical Properties of Carbon Nanotubes* (London: Imperial College Press)
[3] Fan S S, Chapline M G, Franklin N R, Tombler T W, Cassell A M and Dai H J 1999 *Science* **283** 512
[4] Deheer W A, Chatelain A and Ugarte D 1995 *Science* **270** 1179
[5] Murakami Y, Chiashi S, Miyauchi Y, Hu M H, Ogura M, Okubo T and Maruyama S 2004 *Chem. Phys. Lett.* **385** 298
[6] Hata K, Futaba D N, Mizuno K, Namai T, Yumura M and Iijima S 2004 *Science* **306** 1362
[7] Andrews R, Jacques D, Rao A M, Derbyshire F, Qian D, Fan X, Dickey E C and Chen J 1999 *Chem. Phys. Lett.* **303** 467
[8] Ren Z F, Huang Z P, Xu J W, Wang J H, Bush P, Siegal M P and Provencio P N 1998 *Science* **282** 1105
[9] Rao C N R, Sen R, Satishkumar B C and Govindaraj A 1998 *Chem. Commun.* **15** 1525
[10] Sen R, Govindaraj A and Rao C N R 1997 *Chem. Phys. Lett.* **267** 276
[11] Wei B Q, Vajtai R, Jung Y, Ward J, Zhang R, Ramanath G and Ajayan P M 2003 *Chem. Mater.* **15** 1598
[12] Jung Y J, Wei B Q, Vajtai R, Ajayan P M, Homma Y, Prabhakaran K and Ogino T 2003 *Nano Lett.* **3** 561
[13] Wei B Q, Vajtai R, Jung Y, Ward J, Zhang R, Ramanath G and Ajayan P M 2002 *Nature* **416** 495
[14] Zhang Z J, Wei B Q, Ramanath G and Ajayan P M 2000 *Appl. Phys. Lett.* **77** 3764
[15] Zhang Z J, Zhou Y and Yue Y 2005 *Appl. Phys. Lett.* **87** 223121
[16] Xiang R, Luo G H, Qian W Z, Zhang Q, Wang Y, Wei F, Li Q and Cao A Y 2007 *Adv. Mater.* **19** 2360
[17] Xiang R, Luo G H, Qian W Z, Wang Y, Wei F and Li Q 2007 *Chem. Vapor Depos.* at press (doi:10.1002/cvde.200704249)
[18] Chen Y and Yu J 2005 *Appl. Phys. Lett.* **87** 033103
[19] Cao J M 2006 *Appl. Surf. Sci.* **253** 2460
[20] Yue Y, Zhang Z J and Liu C 2006 *Appl. Phys. Lett.* **88** 263115
[21] Okamoto H and Massalski T B 1990 *Binary Alloy Phase Diagrams* 2nd edn (Materials Park, OH: ASM International)
[22] Istratov A A, Hieslmair H and Weber E R 1999 *Appl. Phys.* A **69** 13
[23] Zhong G F, Iwasaki T, Robertson J and Kawarada H 2007 *J. Phys. Chem.* B **111** 1907
[24] Cao A Y, Zhang X F, Xu C L, Liang J, Wu D H and Wei B Q 2001 *Appl. Surf. Sci.* **181** 234
[25] Xiang R, Yang Z, Zhang Q, Luo G H, Qian W Z, Wei F, Kadowaki M and Maruyama S 2007 arXiv:0708.0061v1