

Growth of semiconducting enriched SWCNT on ST-cut quartz substrates by chemical vapor deposition

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Single wall carbon nanotubes (SWCNTs) got attracted widespread attention,[1] due to their electrical and physical exceptional properties.[2] Closely packed arrays of parallel SWCNT have been attractive candidates for the future nanoelectronics,[3,4] because of their exceptional properties, including high mobility and the relatively large currents that they can sustain.[5,6] The next industrial generation of CNT-based nanoelectronics is hampered by several major problems, despite the outstanding performance of individual CNT-based devices.[7] Such challenges include the lack of reliable methods to control the alignment and position of the as-grown nanotubes and simultaneous growth of metallic and semiconducting nanotubes.[8] Controlling spatial position and structural selectivity during the synthesis would thus be beneficial for many of the potential applications of SWCNTs.[6] Significant improvements have been shown regarding the development of reliable routes for growing in-place well aligned SWCNT on different types of substrates using chemical vapor deposition (CVD) process.[6,7] CVD is proven to be the most versatile and promising technique due to upscale possibility and technology compatibility.[3,9] In parallel, researchers have shown successful separation of metallic and semiconducting CNTs by applying solvents-based routes.[10] However, such routes have many drawbacks, as the attractive CNT properties are altered due to the necessary hard treatment steps.[6] Such process essentially introduces defects and shortens the resultant nanotubes. Alternatively, CVD is thought to be a significant approach for the in-place growth of type-selective SWCNT.[11] On the other hand, the coexistence of metallic and semiconducting nanotubes in such samples is still a problem and should be overcome before real industrial integration of CNT in device fabrication. It was shown that horizontally aligned semiconducting-rich SWCNT can be grown on single crystal ST-cut quartz substrates by using optimized CVD process.[7] The actual mechanisms behind the sc-enrichment is still an open question, i.e. is it a CVD process effect or due to the forces taking place between the grown CNTs and the

surface atoms of the support substrate. In the case of CVD process effect, that is extremely positive and opens a window where the route can be further developed toward growth of pure sc-SWCNT or even single chirality SWCNT. If it is a CNT-substrate attraction effect, a detailed and systematic study is required in order to understand the effect of such attraction on the electrical properties of the grown nanotubes. More precisely, does the CNT-substrate attraction affect the performance of electronic devices later fabricated with such CNT?

In this study, we aimed for deeper understanding of the actual mechanisms behind the sc-enrichment CNT grown by CVD. We performed a systematic study, in which we grow SWCNT by CVD on different support substrates under a variety of process conditions. The grown CNT are either lattice-oriented in the case of ST-cut quartz substrates and sapphire substrates or randomly oriented when silicon substrates were used. The variety of the investigated CVD parameters, i.e. catalyst materials and C precursor, allows for thorough understanding resulting in realistic conclusions.

Representative SEM micrographs of the as-grown SWCNT using binary catalyst system (Fe:Co = 2:1 atomic ratio) on different substrates, i.e. ST-cut quartz and sapphire, are shown in figure 1. Both substrates allow growth of horizontally aligned nanotubes, despite that on sapphire the alignment is not perfect as on ST-quartz.[6] The as-grown CNT were transferred onto silicon target substrates using pre-optimized protocol for further characterization.[9] It was advantageous to transfer the grown nanotubes onto substrate, so that the Raman signal from them does not overlap with the that from support substrate as in the case of quartz and sapphire. Three factors were investigated here, the catalyst nanoparticles (binary system), the C precursor and the support substrate. Ethanol was used as the main C precursor, while methanol was introduced as OH radicals supplier. It is believed that these radicals can effectively etched the m-CNT due to their smaller ionization potential compared to s-CNT,[12] in addition to prevent formation of amorphous carbon on the

nanotubes as well on the substrate.[7] Typical Raman spectra of the transferred CNT onto Si substrates, originally grown on ST-cut quartz with different C precursor combination, i.e. Ar bubbles through ethanol and Ar bubbles through methanol, are shown in figure 2.a. It is obvious that the RBM peaks become sharper and stronger as methanol percentage is increased, indicating a positive effect of methanol toward enrichment of s-CNT. In addition, the number of the RBM peaks becomes smaller. This indicates growth of CNT with narrower diameter distribution.[13] The analysis of the Raman spectra collected for CNT grown on different substrates (figure 2.b), with optimized ethanol:methanol ratio for enriched s-CNT samples, reveals that rich s-CNT samples were obtained when using crystalline substrates, i.e. quartz and sapphire, while mixture of m- and s-CNT, with improved ratio, obtained on the silicon substrates. However, the RBM peaks suggest that the CNT grown on quartz are with narrower diameter distribution than those grown on sapphire. These observations were confirmed when characterizing the grown CNTs under different growth conditions with the 633 nm excitation line.

In summary, it is more likely that the growth selectivity is attributed to the effect of process parameters, and secondly to the attraction forces between the grown CNT and the support substrates. Systematic identification of m- and s-CNT in scanning electron microscopy [14] along with the electrical performance of thin film transistors fabricated with the as-grown nanotubes under different conditions allow for better understanding and realistic conclusions..

References

- [1] Q. Wen, W. Qian, J. Nie, A. Cao, G. Ning et al, *Adv. Mater.* 22 (2010) 1867.
- [2] S. J. Tans, A.R.M.; Verschueren, C. Dekker, *Nature* 393 (1998) 49.
- [3] S. J. Kang, C. Kocabas, Ozel, M. Shim, N. Pimparkar et al, *Nature nanotech.* 2 (2007) 230.
- [4] Z. Chen, J. Appenzeller, Y.M. Lin, J. Sippel-Oakley, A. G. Rinzler et al, *Science* 311 (2006) 1735.
- [5] N. Rouhi, D. Jain, K. Zand, P. J. Burke, *Adv. Mater.* 23 (2011) 94.
- [6] I. Ibrahim, A. Bachmatiuk, J. H. Warner, B. Büchner, G. Cuniberti et al, *Small* 8 (2012) 1973.
- [7] L. Ding, A. Tselev, J. Wang, D. Yuan, H. Chu et al, *Nano Lett.* 9 (2009) 800.
- [8] W. Kim, H.C. Choi, M. Shim, Y. Li, D. Wang et al, *Nano Lett.* 2 (2002) 703.
- [9] I. Ibrahim, A. Bachmatiuk, F. Börrnert, J. Blüher, S. Zhang et al, *Carbon* 49 (2011) 5029.
- [10] R. Krupke, F. Hennrich, H. v. Löhneysen, M.M. Kappes, *Science* 301 (2003) 344.
- [11] X.L. Li, L. Zhang, X.R. Wang, I. Shimoyama, X.M. Sun et al, *J. Am. Chem. Soc.* 129 (2007) 4890.
- [12] J. Lu, S. Nagase, X.W. Zhang, D. Wang, M. Ni et al, *J. Am. Chem. Soc.* 128 (2006) 5114.
- [13] Y. Che, C. Wang, J. Liu, B. Liu, X. Lin et al, *ACS Nano* 6 (2012) 7454.
- [14] J. Li, Y. He, Y. Han, K. Liu, J. Wang, Qunqing Li et al, *Nano Lett.* 12 (2012) 4095.

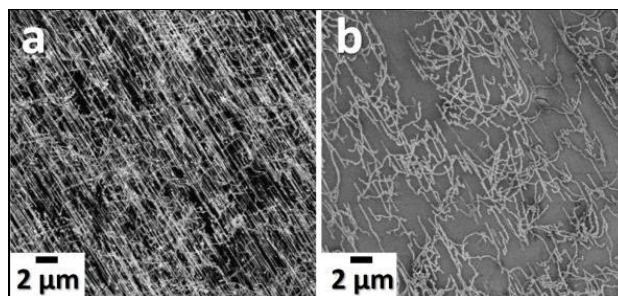


Figure 1. Growth of SWCNT: Representative SEM images of as-grown CNT on a. ST-cut quartz and b. sapphire.

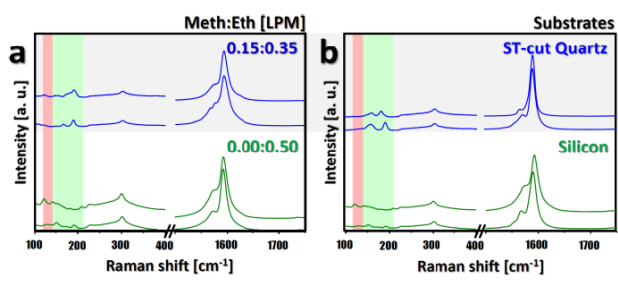


Figure 2. Effect of process parameters: Raman spectra for the a. CNT grown on ST-cut quartz with different C precursor combination and later transferred onto Si substrate, and b. CNT grown on different substrates with Eth:Meth = 0.25:0.25 LPM. [515 nm excitation line was used. All spectra were normalized to the G mode of the same signal]