Growth of high yield metallic-free horizontally aligned single wall carbon nanotubes nucleated from fullerene

Imad Ibrahim,[1,2] Alicja Bachmatiuk,[1] Bernd Büchner,[1] Mark H. Rümmeli,[1] Gianaurelio Cuniberti[2]

1 IFW Dresden, P.O. Box 270116, 01171 Dresden, Germany
2 Technische Universität Dresden, D-01062, Dresden, Germany

imad.ibrahim@ifw-dresden.de

Abstract

Since the pioneering work in 1991 by Iijima,[1] single wall carbon nanotubes (SWCNTs) have attracted widespread attention.[2,3,4] Their exceptional electrical and physical properties motivate intense research in order to integrate them in to different applications.[5] Typical applications include, field effect transistors,[6] thin film transistors,[7] logic circuits,[8] and bio, environmental and medical sensors.[9] Horizontally aligned SWCNTs, where spatial position, orientation, yield are controlled, are essential for large-scale electronics.[10, 11] Different methods, such as laser ablation and arc-discharge can be used to grow SWCNTs which can be aligned post-synthesis using different techniques.[12] However, such routes provide short and defective aligned SWCNTs. In the contrast, chemical vapor deposition (CVD) can be used to grow long, defect-free and clean horizontally aligned SWCNTs in a single step,[13] in addition to its simplicity and up-scalability.[14] Accordingly, CVD has become the most promising and common method for growing aligned SWCNTs on different substrates over a wide range of growth parameters.[15,16] Nevertheless, there are still challenges that should be overcome prior to integrating horizontally aligned SWCNTs in nanoelectronic applications, including the growth of tubes with a homogenous diameter, chirality and electrical properties. Growth of metallic-free horizontally aligned SWCNTs is also advantageous due to avoidance of metal diffusion into the chip which can lead to device degradation. Metal-free SWCNTs were grown on scratched or treated quartz and silicon substrates nucleated from SiO_2 nanoparticles,[17] Al_2O_3 and TiO_2.[18]. More recently, growth of catalyst-free SWCNTs was demonstrated. Cloning short carbon nanotubes working as seeds in CVD reaction is an example.[19] It is shown also that functionalized open caps fabricated from fullerene-based structures may nucleate the carbon nanotube growth.[20]

In this study, we grow metallic-catalyst-free horizontally aligned SWCNTs nucleated by functionalized hemispherical caps prepared from different fullerene-based structures. Pristine fullerene (C_{60}) were dispersed in different solvents; including, toluene, acetone, ethanol and methanol, and sonicated over night to ensure better dispersion. Drops of fullerene solvents were loaded to stable temperature (ST-) cut single crystal quartz substrates. The ST-cut quartz substrates were subjected to thermally annealed prior the CVD in order to have very smooth surface, which has been shown to enhance the yield of the later grown tubes.[11] The loaded substrates were treated under different conditions resulting functionalized hemispherical opened-caps, followed by the CVD reaction using ethanol as the carbon precursor.

The yield of the grown tubes is tuned and enhanced by changing the thermal pre-treatment temperature, period and environment for the fullerene structure prior the CVD reaction. We found that an optimized thermal treatment period leads to higher yields, indicating that such pre-treatment produces higher numbers of hemispherical caps appropriate for tube nucleation. Moreover, treating the fullerene structures in low oxygen environments (e.g argon) increases the tube yield. In figure 1.a, one can see the plot of the CNTs yield variation based on the thermal treatment period. It is shown in the plot that the yield goes through a maximum with thermal period of 75 minutes; farther treatment decreases the achieved yield due to excess destruction of the fullerene clusters. The environment in which the thermal treatment is performed is another important factor which strongly affects the yield of the grown CNTS. Thermal treatment of the fullerene clusters in a low oxygen environment slows down the burning rate leaving more fullerene segments attached to the clusters. Figure 1.b summarizes the effect of this parameter on the as-grown tubes yield. In addition, the choice of solvent in which the fullerenes are dispersed affects the formed fullerene cluster size and possible functionalization, and hence affect the tubes yield. It was found that despite toluene being the best dispersion solvent for fullerenes as compared to other solvents, it gave the lowest yield of grown tubes. While acetone gave the highest yield although it is a bad solvent for fullerene dispersion. This suggests that the choice of solvent affects the size of the formed fullerene cluster, which dramatically increases the effective area where successful nucleation can take place and also determines the possible functional groups which can be attached to the opened fullerene. Characterization of the as-grown tubes with (AFM) shows that an existed tip (cluster) at one end of the tube, as shown in figure 2. Characterization of many such

tubes with AFM allowed us to plot the tubes diameter distribution as well as the corresponding cluster diameter as shown in the insert in figure 2. One can see that the obtained CNTs diameter distribution is quantized in well defined steps. In addition, there is no direct relation between the tube and the cluster diameters. Also, the AFM data suggest that the grown tubes are single wall CNTs, which is also confirmed with Raman spectroscopy. Systematic studies of the fullerene structure after different treatment steps as well as after tubes growth allow us to speculate a nucleation and growth mechanism for such metal-free SWCNTs.

References

[1] S. Iijima, Nature **354** (1991) 56.
[2] P. Avouris, Acc. Chem. Res. **35** (2002) 1026.
[3] V. N. Popov, Mater. Sci. Eng, R **43** (2004) 61.
[4] Q. Cao, J. A. Rogers, Adv. Mater. **21** (2009) 29.
[5] R. Saito, G. Dresselhaus, M. S. Dresselhaus, Physical properties of carbon nanotubes. Imperial College press: London, 1998
[6] S. J. Tans, A. R. M. Verschueren, C. Dekker, Nature **393** (1998) 49.
[7] S. J. Kang, C. Kocabas, T. Ozel, M. Shim, N. Pimparkar, M. A. Alam, S. V. Rotkin, J. A. Rogers, Nature nanotechnol. **2** (2007) 230.
[8] Z. Chen, J. Appenzeller, Y. M. Lin, J. Sippel-Oakley, A. G. Rinzler, J. Tang, et al, Science **311** (2006) 1735.
[9] M. Briman, E. Artukovic, L. Zhang, D. Chia, L. Goodglick, G. Gruner, Small **3** (2007) 758.
[10] N. Ishigami, H. Ago, K. Imamoto, M. Tsuji, K. Iakoubovskii, et al, J. Am. Chem. Soc. **130** (2008) 9918.
[11] I. Ibrahim, A. Bachmatiuk, F. Börrnert, J. Blüher, S. Zhang, et al, Carbon **49** (2011) 5029.
[12] R. Krupke, S. Linden, M. Rapp, F. Hennrich, Adv. Mater. **18** (2006) 1468.
[13] S. J. Kang, C. Kocabas, T. Ozel, M. Shim, N. Pimparkar, M. A. Alam, S. V. Rotkin, J. A. Rogers, nature nanotech. **2** (2007) 230.
[14] S. Dittmer, J. Svensson, E. E. B. Campbell, Current Applied Physics **4** (2004) 595.
[15] C. Kocabas, S.-H. Hur, A. Gaur, M. A. Meit, M. Shim, J. A. Rogers, Small **1** (2005) 1110.
[16] Z. Jin, H. Chu, J. Wang, J. Hong, W. Tan, Y. Li, Nano Lett. **7** (2007) 2073.
[17] B. Li, X. Cao, X. Huang, G. Lu, Y. Huang, et al, small **5** (2009) 2061.
[18] S. Huang, Q. Cai, J. Chen, Y. Qian, L. Zhang, J. Am. Chem. Soc. **131** (2009) 2094.
[19] Y. Yao, C. Feng, J. Zhang, Z. Liu, Nano Lett. **9** (2009) 1673
[20] I. Ibrahim, A. Bachmatiuk, M. H. Rümmeli, U. Wolff, A. Popov, et al, Phys. Status Solidi B **248** (2011) 2467.

Figures

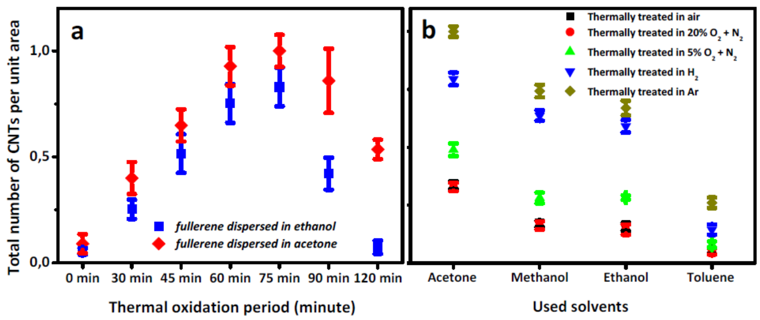

Figure 1: Grown tubes yield dependency on the thermal treatment **a**) period **b**) environment

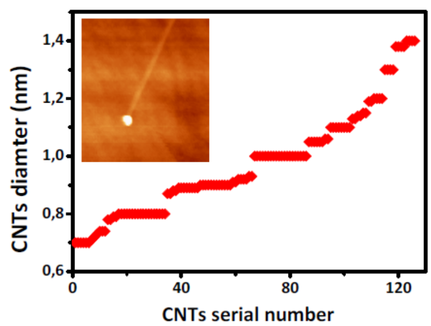

Figure 2: CNT height distribution of the fullerene-nucleated CNTs, (inset) AFM image for cluster at the end of fullerene-nucleated SWCNT