Phys. Status Solidi B **248**, No. 11, 2467–2470 (2011) / **DOI** 10.1002/pssb.201100073

physica status solidi b
www.pss-b.com
basic solid state physics

Growth of catalyst-assisted and catalyst-free horizontally aligned single wall carbon nanotubes

Imad Ibrahim*[,1,2], Alicja Bachmatiuk[1], Mark H. Rümmeli[1], Ulrike Wolff[1], Alexey Popov[1], Olga Boltalina[3], Bernd Büchner[1], and Gianaurelio Cuniberti[2]

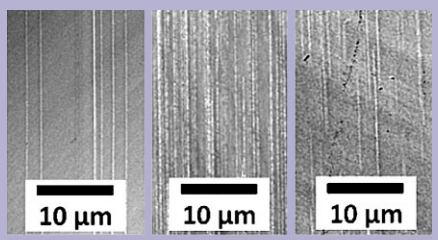
[1] IFW Dresden, P.O. Box 270116, 01171 Dresden, Germany
[2] Technische Universität Dresden, 01062 Dresden, Germany
[3] Colorado State University, Fort Collins, 80523 Colorado, USA

Received 29 April 2011, revised 30 June 2011, accepted 19 July 2011
Published online 11 August 2011

Keywords carbon nanotubes, catalytically grown carbon, CVD, fullerene nucleated CNT

* Corresponding author: e-mail i.ibrahim@ifw-dresden.de, Phone: +49 (0)351 4659-300, Fax: +49 (0)351 4659-313

Here, we report the growth of homogenously horizontally aligned single wall carbon nanotubes on stable temperature cut single crystal quartz using chemical vapor deposition with controllable yield and length from binary metallic mixtures as well as fullerene derivatives. We manage the yield and length of the as-grown tubes on stable temperature cut single crystal quartz by controlling the surface roughness of the support substrates by thermal treatment in air. Carbon caps derived from pre-treated fullerenes are also explored for their potential to nucleate growth of single wall carbon nanotubes without the need of a catalyst particle. Exohedrally functionalized fullerenes are apparently better nucleators than C_{60} fullerenes.



Yield of the as-grown single wall carbon nanotubes on thermally annealed ST-quartz substrates.

1 Introduction Spatial control and yield of horizontally aligned single wall carbon nanotubes (SWCNTs) [1, 2] in combination with attractive physical and electronic properties for SWCNTs make them promising candidates for next generation nanoelectronics [3, 4]. Chemical vapor deposition (CVD) is often used for the growth of horizontally aligned SWCNTs. Depending on the synthesis parameters and the choice of substrate (e.g., stable temperature (ST)-cut single crystal quartz substrates which have a (0111) crystallographic plane with their surface normal lying close to 38° from the y axis ([010])) different yields, and alignment directions can be obtained [5–7]. In one approach, different metallic catalyst nanoparticles or mixtures of metals are used to nucleate the growth of the CNTs in a single or successive CVD process in order to increase the yield of the grown tubes [7–9]. Another technique involves pre-annealing of the catalyst support [10, 11]. However, the procedure is not well understood. Here, we explore increasing the yield of as-grown SWCNTs by the thermal annealing of ST-cut quartz supports in a controllable manner prior to the CVD process. Our findings show that the thermal annealing affects the substrates' surface roughness which in turn affects the size distribution of the formed metallic catalyst nanoparticles residing on the substrates. As a result, the surface roughness and the catalyst size distribution affect the yield of the grown SWCNTs on the annealed substrates. Growth of metal-catalyst-free SWCNTs nucleated from fullerene derivatives is also shown. These tubes overcome the negative effect of metal catalyst diffusion when using SWCNTs as a building block for electronic devices. Our results show that modified fullerenes (with exohedral fluorine atoms) lead to higher yields of grown SWCNTs than obtained with pure C_{60}.

2 Experimental part

2.1 ST-cut quartz substrates thermal annealing Stable temperature (ST)-cut single crystal quartz polished wafers of 10 cm diameter, 0.5 mm thickness with an angle cut of 38°00′ (Hoffman Materials, LLC) were cut into square small pieces (5 mm × 5 mm). These substrates were subjected to thermal annealing in air under atmospheric pressure at 750 °C for different periods in the range of 10 min until 48 h.

2.2 Growth of catalyst-assisted SWCNTs Binary metallic catalyst systems consisting of different ratios of Fe and Co drop coated on the annealed ST-cut quartz substrates were used for the growth of SWCNTs. The mixtures were prepared from ferrocene (Sigma Aldrich, ≥98%) and cobalt (II) phthalocyanin (Fluka Chemie, >97%) with a total concentration of 0.01%. In order to characterize the formed catalyst nanoparticles on the annealed substrates, the catalyst-loaded substrates were heated in a 1 inch quartz tube in 0.1 LPM (Litre per Minute, 1/min) flow of H_2 toward 950 °C, then the power was turned off and the catalyst-loaded substrates cooled naturally in a H_2 environment. Later, the formed catalysts height was measured with atomic force microscopy (AFM from Digital instruments DI 3100) performed in tapping mode. The catalyst was also prepared in the same manner for the growth of SWCNTs, and heated in H_2 flow of 0.1 LPM toward 950 °C, after reaching this temperature, the H_2 flow rate was reduced to 0.013 LPM and methane was introduced with a flow rate of 1.12 LPM, after 15 min the gas flow stopped and the reactor was evacuated with a membrane pump while the oven cooled down to room temperature.

2.3 Growth of catalyst-free SWCNTs Fullerene-based structures including C_{60} and fluorofullerene $C_{60}F_{18}$ were used to nucleate the growth of CNTs. The growth process was based on a procedure introduced elsewhere [12]. Firstly, fullerene-based structures were dispersed in toluene and drop coated on annealed ST-cut quartz substrates for 15 h at 750 °C (as these have the smoothest surfaces). Nucleation caps are formed from these dispersed fullerene-based structures upon heating in air under atmospheric pressure for 1 h at different temperatures in the range of 400–500 °C and then cleaned from any amorphous carbon by introducing Ar (0.17 LPM) gas bubbles through water while the oven temperature is 900 °C. Then the caps were activated by removing the functional groups from them with introducing H_2 with flow rate of 0.76 LPM for 3 min while the oven temperature is 900 °C. CNTs were grown in a mixture of Ar (0.1 LPM) bubbles through ethanol and H_2 (0.2 LPM) for 20 min at atmospheric pressure and 900 °C.

Fullerene-nucleated SWCNTs are more attractive and promising for future nanoelectronics since no metal catalyst is required, although growth of catalyst-assisted CNTs are easier, since producing open cap from fullerene-structures is more difficult than activation the catalyst nanoparticles.

3 Results

3.1 Morphological characterization of thermally annealed ST-cut quartz substrates ST-cut quartz substrates were annealed in air at 750 °C for different periods between 10 min and 48 h. Figure 1a–c shows typical surface topography for the various annealed substrates. It is shown that for short annealing periods the surface remains rough with narrow shallow pits. Gradually the surface gets smoother with increased annealing going through a minimum after which the surface gets rough again with deep, broad and regular pits. The optimum annealing period for smooth substrate surfaces is ca. 15 h. The plot in Fig. 1d confirms that the substrates annealed for 15 h are the smoothest with lowest surface average roughness, while other annealed substrates for longer or shorter periods are rougher.

3.2 Size distribution of the formed metallic catalyst The size distribution for the metallic catalyst from different mixtures formed on the annealed substrates for different periods is shown in Fig. 2. Generally, the mean size of the formed nanoparticles increases and the size distribution broadens as the annealing period is extended. This may be related to the surface morphology [13] where shallow narrow pits in the surface lead to small catalyst nanoparticles formed on the short period-annealed substrates, whereas

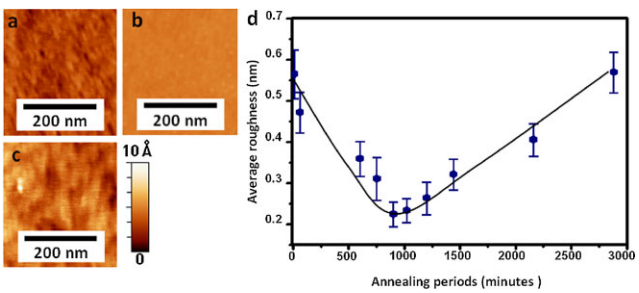


Figure 1 (online color at: www.pss-b.com) Taping mode AFM images for the ST-cut quartz substrates exposed to different thermal annealing (a) 5 h, (b) 15 h and (c) 24 h, (d) annealed ST-cut quartz substrates surface roughness time dependence.

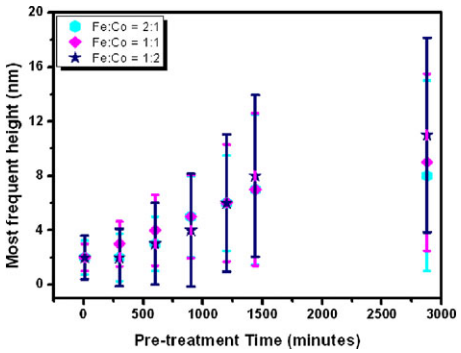


Figure 2 (online color at: www.pss-b.com) Size analysis of formed binary metallic catalyst on annealed ST-cut quartz substrates thermally treated in H_2 flow.

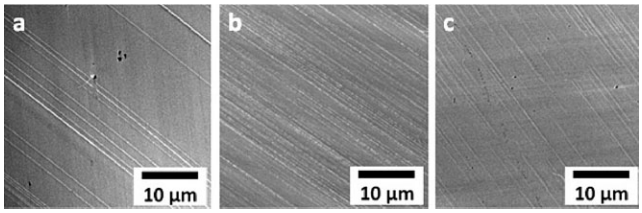


Figure 3 Yield of the binary metallic catalyst-assisted as-grown CNTs on thermally annealed ST-quartz substrates (a) 10 min, (b) 15 h, and (c) 48 h.

deep broad pits on the long period-annealed substrates related to large catalyst nanoparticles. Our findings show no observable effect with different metallic mixtures which is in agreement with other studies [9].

3.3 As-grown metallic-catalyst-assisted SWCNTs Carbon nanotubes (CNTs) were grown on ST-cut quartz substrates subjected to various thermal annealing for different periods from different catalyst mixtures. Figure 3 shows typical SEM images for the as-grown CNTs which show that the highest possible CNTs yield is on the substrates annealed for 15 h which have the smoothest surfaces. It is not only the yield of the grown tubes which is affected, but also their length. The average length of tubes grown on the smoothest surfaces is larger than 100 μm, while those grown on rough surfaces range between 20 and 60 μm in most cases. AFM was implemented to determine the diameter (height) distribution of the tubes/bundles. The height distribution of the CNTs grown on ST-cut quartz substrates from different metallic catalyst ratios is shown in Fig. 4. The data reveal the tubes diameter (or bundles) is between 0.8 and 1.7 nm with no dependency on neither the thermal annealing period nor the catalyst mixtures ratio [9]. Moreover, no effect on yield is observed between the different catalyst mixtures explored.

The grown tubes were also characterized by TEM as well as Raman spectroscopy. The results are shown in Fig. 5. The presence of a strong and narrow G mode (tangential phonon modes), high G/D ratio (crystallinity) and the well-known

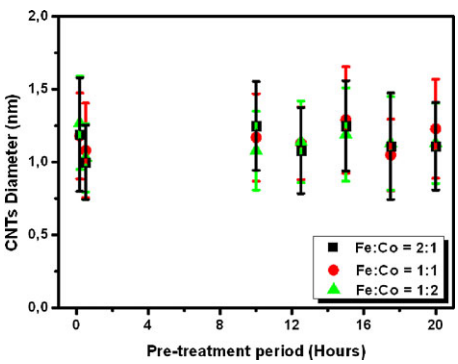


Figure 4 (online color at: www.pss-b.com) Height distribution of the binary metallic catalyst-assisted as-grown CNTs over annealed ST-cut quartz substrates.

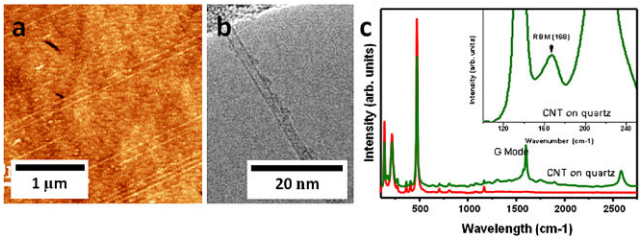


Figure 5 (online color at: www.pss-b.com) (a) AFM taping mode image for the as-grown SWCNTs, (b) TEM micrograph shows SWCNT from the grown tubes transferred to a TEM cupper grid, and (c) typical Raman signal for the as-grown SWCNTs on ST-cut quartz substrates from a metallic mixture of Fe:Co with a ratio 1:2.

RBM (radial breathing modes) modes suggest that the grown tubes are SWCNTs [14]. Data from TEM studies confirm that the samples consist homogenously of SWCNTs.

3.4 As-grown catalyst-free SWCNTs C_{60} and fluorofullerene $C_{60}F_{18}$ were also explored for their potential to nucleate the growth of CNTs on ST-cut quartz substrates in a modified CVD process similar to that described elsewhere [12]. An initial thermal oxidation in air followed by a cleaning process to remove the amorphous carbon using water vapor and finally activation of the opened caps in an H_2 environment was performed prior to the CVD reaction. Thereafter the CVD reaction is applied. The results from the samples prepared showed higher yields of SWNT are obtained from fluorofullerene oxidized at lower temperature (450 °C) than C_{60} which required oxidation at higher temperatures (500 °C) as shown in Fig. 6. C_{60} fullerenes showed a yield dependence with oxidation temperature, increasing with temperature, in agreement with Yu et al. [12].

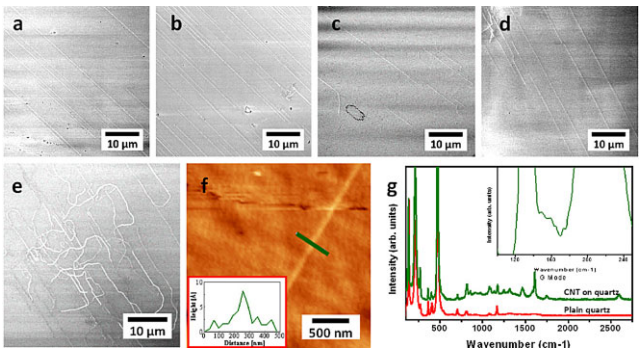


Figure 6 (online color at: www.pss-b.com) SEM images for the SWCNTs nucleated form fluorofullerene where the thermal oxidation temperature was (a) 400 °C, (b) 450 °C, and (c) 500 °C. SEM images for the SWCNTs nucleated form fullerene using thermal oxidation temperature (d) 450 °C and (e) 500 °C. (f) AFM image of an individual as-grown SWCNT on annealed ST-cut quartz nucleated from fluorofullerene $C_{60}F_{18}$ thermally oxidized at 450 °C (inset: height profile for the shown SWCNT). (g) Typical Raman signal for the as-grown SWCNTs on annealed ST-cut quartz substrate nucleated from pretreated-fullerenes (75 min in air at 450 °C).

4 Discussion

4.1 ST-cut quartz substrates surface roughness effect on the catalyst-assisted SWCNTs growth One possible reason behind the thermal annealing effect is that; ST-cut quartz substrates gain energy at elevated temperatures, which forces the surface atoms to rearrange themselves towards a new energy minimum [15]. Some surface atoms escape due to the extra gained energy. The process of surface atom rearrangement and atoms escaping decreases the surface roughness after a specific period of annealing, which is 15 h under our experimental conditions. Further annealing in air causes extra energy transfer to the substrate leading to bond breakage and atom displacement [16], which causes the substrate surface to become rough again [17]. The surface morphology affects the size of the formed metallic catalyst nanoparticles and hence they will depend on the annealing process. As a general trend a broadening of the nanoparticles size distribution is observed as the annealing period increases. In the CVD process, where the temperature is 950 °C, those particles melt and break up into smaller ones which later will nucleate the SWCNTs growth [18, 19]. This process is easier on smooth surfaces than on rough surfaces where the nanoparticles are trapped within the pits hindering successful tube nucleation. In other words the particles are required to break up into smaller particles to nucleate the CNT. At elevated temperatures, as in the case of our CVD reaction, quartz substrates adopt the ß-phase, where the surface atoms preferentially align in the *x*-direction ([100]) producing channels [10]. It is believed that the SWCNTs will later grow with directional preference along such channels. It is more likely that those channels are long and well-aligned in the case of smooth surfaces, which leads to the growth of long, dense and well-aligned SWCNTs. Rough surfaces disturb the aligned growth process.

4.2 Fullerene-based structures nucleated growth of SWCNTs Growing SWCNTs from fullerene-based structures requires they be opened first. This was achieved by thermally oxidizing them in air for 1 h. It was possible to grow a higher yield of SWCNTs from fluorofullerene (oxidized at 450 °C) as compared to C_{60}. C_{60} fullerenes required higher oxidation temperatures to grow SWCNTs. This is presumably because the fluorine atoms bonded to the adjacent carbon atoms of the fullerene cage enforce dramatic elongation of C–C bonds, which therefore break more easily [20, 21].

5 Conclusion

We have shown that thermal annealing of ST-cut quartz substrates in air affects the surface morphology. Competing mechanisms occur so that a minimum surface roughness occurs after 15 h annealing at 750 °C. The greatest yields and lengths of SWCNT are obtained with these optimized annealed substrates. We also explore fullerenes as an alternative to metal catalyst grow SWCNT. Exohedrally functionalized fluorofullerenes are apparently better to nucleate SWCNT since they are more readily opened as initial nucleation caps for SWCNT growth.

Acknowledgements MHR thanks the EU (ECEMP) and the Freistaat Sachsen, II the DAAD (A/07/80841), AB the Alexander von Humboldt Foundation and the BMBF, GC acknowledges support by the World Class University program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology.

References

[1] N. Ishigami, H. Ago, K. Imamoto, M. Tsuji, K. Iakoubovskii, and N. Minami, J. Am. Chem. Soc. **130**, 9918 (2008).
[2] I. Ibrahim, A. Bachmatiuk, F. Börrnert, J. Blüher, U. Wolff, J. H. Warner, B. Büchner, G. Cuniberti, and M. H. Rümmeli, Carbon (2011), DOI: 10.1016/j.carbon.2011.07.020.
[3] R. Saito, G. Dresselhaus, and M. S. Dresselhaus, Physical Properties of Carbon Nanotubes (Imperial College Press, London, 1998).
[4] Q. Wen, W. Qian, J. Nie, A. Cao, G. Ning, Y. Wang, L. Hu, Q. Zhang, J. Huang, and F. Wei, Adv. Mater. **22**, 1867 (2010).
[5] W. Zhou, C. Rutherglen, and B. J. Burke, Nano Res. **1**, 158 (2008).
[6] T. P. McNicholas, L. Ding, D. Yuan, and J. Liu, Nano Lett. **9**(10), 3646 (2009).
[7] D. Yuan, L. Ding, H. Chu, Y. Feng, T. P. McNicholas, and J. Liu, Nano Lett. **8**(8), 2576 (2008).
[8] Y. Li, W. Kim, Y. Zhang, M. Rolandi, D. Wang, and H. Dai, J. Phys. Chem. B **105**, 11424 (2001).
[9] W. Zhou, L. Ding, and J. Liu, Nano Res. **2**, 593 (2009).
[10] A. Rutkowska, D. Walker, S. Gorfman, P. A. Thomas, and J. V. Macpherson, J. Phys. Chem. C **113**, 17087 (2009).
[11] J. Xiao, S. Dunham, P. Liu, Y. Zhang, C. Kocabas, L. Moh, O. Huang, K.-C. Hwang, C. Lu, W. Huang, and J. A. Rogers, Nano Lett. **9**(12), 4311 (2009).
[12] X. Yu, J. Zhang, W. Choi, J.-Y. Choi, J. M. Kim, L. Gan, and Z. Liu, Nano Lett. **10**(9), 3343 (2010).
[13] L. Ratke and P. W. Voorhees, Growth and Coarsening: Ostwald Ripening in Material Processing (Springer, Berlin, 2002).
[14] A. Jorio, R. Saito, J. H. Hafner, C. M. Lieber, M. Hunter, T. McClure, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. Lett. **86**, 1118 (2001).
[15] J. Nye, Physical Properties of Crystals and Their Representation by Tensors and Matrices (Clarendon Press, Oxford, 1985).
[16] J. B. Baldo and W. N. dos Santos, Ceramica **48**(307), 172 (2002).
[17] E. Philippot, D. Palmier, M. Pintard, and A. Goiffon, J. Solid State Chem. **123**, 1 (1996).
[18] A. Mathur, S. S. Roy, M. Tweedie, P. D. Maguire, and J. A. Mclaughlin, J. Nanosci. Nanotechnol. **9**, 4392 (2009).
[19] A. Mathur, S. S. Roy, C. Dickinson, and J. A. McLaughlin, Curr. Appl. Phys. **10**(2), 407 (2010).
[20] I. S. Neretin, K. A. Lyssenko, M. Y. Antipin, Y. L. Slovokhotov, O. V. Boltalina, P. A. Troshin, A. Y. Lukonin, L. N. Sidorov, and R. Taylor, Angew. Chem. Int. Ed. **39**, 3273 (2000).
[21] O. V. Boltalina, B. de La Vaissiere, P. W. Fowler, P. B. Hitchcock, J. P. B. Sandall, P. A. Troshin, and R. Taylor, Chem. Commun. **2000**(14), 1325 (2000).

