

GROWTH OF SINGLE WALLED CARBON NANOTUBES NETWORKS USING Al - Ni AS CATALYST

Mário Kotlár^{1,2}, Viliam Vretenár², Marian Veselý¹, Róbert Redhammer¹

*1. Department of Microelectronics, Slovak University of Technology, Ilkovičova 3, 812 19
Bratislava, Slovakia*

2. Danubia NanoTech, s.r.o., Ilkovičova 3, 841 04 Bratislava, Slovakia

E-mail: mario.kotlar@stuba.sk

Received 30 April 2011; accepted 15 May 2011.

1. Introduction

Carbon nanotube is a cylindrical shaped structure made purely of carbon atoms. Carbon atoms are arranged in a hexagonal crystal lattice. We can consider carbon nanotube as one graphite layer that is rolled up into cylinder having diameter of nanometers and length of micrometers order. Due to their unique structure, carbon nanotubes (CNTs) have many interesting electronic, mechanical and chemical properties. Thanks to their high surface – volume ratio, thermal stability and chemical sensitivity, carbon nanotubes are well suited for detection of chemical vapors. Currently there is no method for precise manipulating and positioning of individual carbon nanotubes and even every growth technique produces carbon nanotubes with different chiralities and diameters.

CNTs are prepared by many techniques but chemical vapor deposition (CVD) is the simplest and probably the most widely technology used for their growth. In this process the thermal decomposition of hydrocarbon is achieved in the presence of metal catalysts on the surface of substrate. The pretreatment and synthesis conditions, as well as morphology and structure of catalytic nanoparticles play an important role in determining both diameter d_t and chirality (n, m) of such synthesized CNTs (Kajiwara, Suzuki, Matsui, Sato, & Hata, 2010). The particle size strongly depends on the catalyst composition and annealing temperature (pretreatment conditions). Ni, Fe, Co or Mo can be used as catalyst because of two main reasons: high solubility of carbon and high carbon diffusion rate in these metals (Kumar & Ando, 2010). In recent years bimetallic catalysts such as Ni-Co, Fe-Co (Ansaldi et al., 2007) and Fe-Mo [4,5] and three-layered catalysts with admixture of Al [6,7] have been reported.

The Al layer promotes the formation of very small bimetallic particles that can catalyze the growth of CNTs. In this work, the effect of pretreatment and synthesis conditions on the growth of carbon nanotubes was studied. Experiments were performed using the thermal CVD apparatus. Bimetallic thin films of Al/Ni have been used as catalytic layer, which led into the synthesis of SWCNTs “networks” (horizontally aligned CNTs).

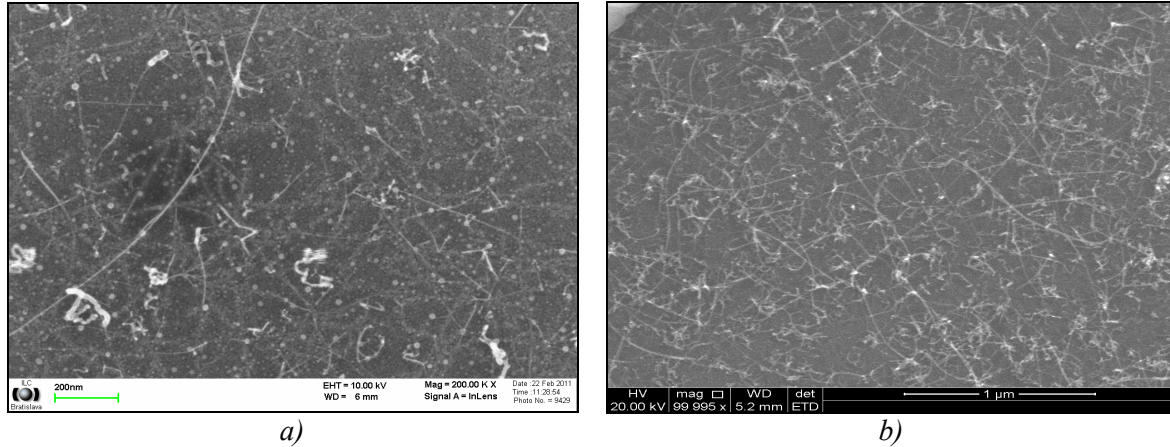


Fig.1: SEM images of SWCNTs networks grown at different temperatures a) 850 °C and b) 900 °C.

2. Experiments

Experiments were carried out in a tube furnace with quartz tube of 40 mm inner diameter. CNTs were grown on small substrates (5x5 mm²) cut off from Si (100) single crystal wafer (n-type) having thermally oxidized surface. Methane (CH₄) was used as a source of hydrocarbons. For the growth of SWCNTs “networks”, Al (8 nm)/Ni (2 nm) two-layered films were evaporated on the SiO₂ surface of substrates. The temperature of the furnace was ramped up to 1000 °C and stabilized. After that the samples were moved into the furnace and annealed in the flow of Ar/H₂ mixture (200/30 sccm) for 10 - 30 min. The growth of carbon nanotubes was performed then in the flow of Ar/H₂/CH₄ mixture (200/30/80 sccm) for 10 min. Both processes (annealing and growing) were run at the same temperature ranging from 750 to 900 °C. After the CNTs growth, the samples were moved out from the center of furnace and the quartz tube was continuously purged with flow of Ar until the temperature reached 90 °C.

3. Results and discussion

After experiments the samples were examined by Raman spectroscopy with 632.8 nm He-Ne laser. The structural morphologies of synthesized CNTs were characterized by scanning electron microscopy (SEM). In Fig. 1, SEM pictures of the SWCNTs networks are shown for different growth temperatures. The SWCNTs network consists of 2D configuration of randomly spread carbon nanotubes. The measured Raman spectra of the SWCNTs samples are depicted as a function of temperature and annealing time (Fig. 2).

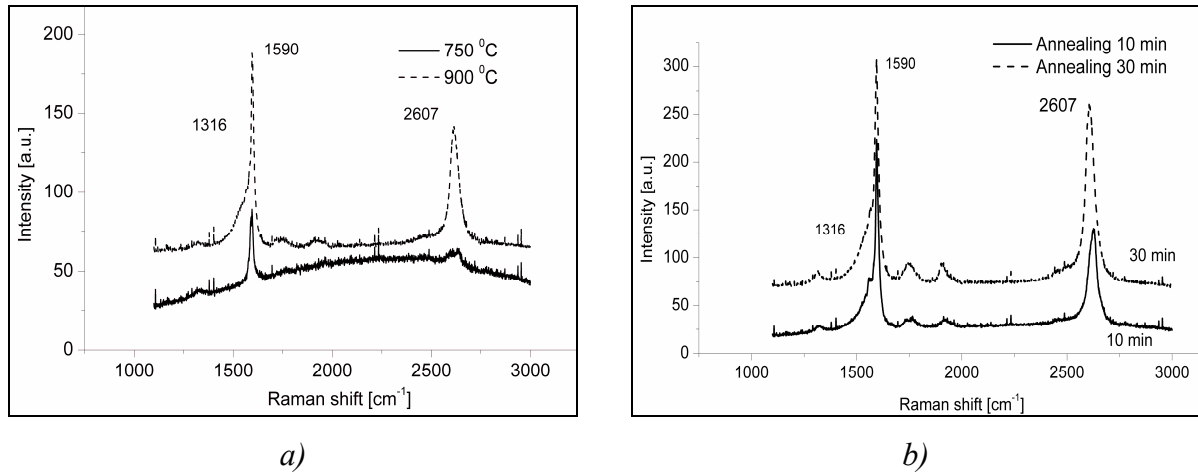


Fig.2: Measured Raman spectrum for different growth temperatures a) and annealing times b)

With the help of Raman spectroscopy, the quality and crystallinity of carbon nanotubes might be characterized. In the upper part of Raman spectrum two strong peaks, G and 2D at position of 1590 cm⁻¹ and 2607 cm⁻¹, respectively, and one weak peak, D at position of 1316 cm⁻¹, can be seen (Fig. 2). The G band is related to the stretching of C - C bonds in two dimensional hexagonal crystal lattice of graphite, whereas the D band is related to the disorder carbon or diamond like carbon structures. The quality of carbon nanotubes is then estimated according to the ratio of these individual peaks, I_D/I_G ratio.

Dependence of I_D/I_G ratio on the temperature (Fig. 2, a) is showing lower values for carbon nanotubes grown at higher temperatures (900 °C), which indicates their better quality in comparison with carbon nanotubes grown at lower temperatures (750 - 800 °C). In the case of Raman spectra as a function of different annealing time, no significant difference is observed (Fig. 2, b).

4. Conclusion

The growth of SWCNTs networks on the SiO₂ chips was examined for different growth temperatures and annealing times. According to Raman spectroscopy the temperature is a significant parameter which affects quality of carbon nanotubes. For higher temperatures (850 - 900 °C) the best quality was achieved. On the other hand, the different annealing times did not affect results of our experiments. SWCNTs network consists of large amount of intersecting carbon nanotubes. This network is electrically conductive over large distances. The SWCNTs networks can be used as transparent conductive layer or as sensitive layer of chemical sensors.

Acknowledgement

This work was done in Center of Excellence CENAMOST (Slovak Research and Development Agency Contract No. VVCE-0049-07) and was financially supported also by grants APVV-0628-06, APVV-0548-07, SK-CZ-0139-09, LPP-0094-09, LPP-0246-06, LPP-0149-09, and VEGA 1/0807/08, 1/0857/08, 1/0746/09, 1/0390/08.

References

- [1] K. Kajiwara, et al.: *Journal of Physics: Conference Series*, **226**, 012008 (2010).
- [2] M. Kumar, et al: *Journal of Nanoscience and Nanotechnology*, **10**, 3739 (2010).
- [3] A. Ansaldo, et al: *Physica E: Low-dimensional Systems and Nanostructures*, **37**, 6 (2007).
- [4] B. Singh, et al: *Solid State Communications*, **144**, 498 (2007).
- [5] C. Chiu, et al: *Surface and Coatings Technology*, **200**, 3199 (2006).
- [6] B. H. Choi, et al: *Microelectronic Engineering*, **87**, 1500 (2010).
- [7] Y. Chen, et al: *Carbon*, **45**, 3007 (2007).