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GROWTH OF MULTI-WALLED CARBON NANOTUBES BY CHEMICAL VAPOR DEPOSITION

S.A. Moshkalyov[1*]; C. Reyes-Betanzo [1,2]; A.C.S. Ramos[3]; J.L. Gonçalves[1]; J. W. Swart[1,2]
[1] Centro de Componentes Semicondutores (CCS)
[2] Faculdade de Engenharia Elétrica e de Computação (FEEC)
[3] Departamento de Fisica Aplicada - DFA, IFGW
C.P. 6061
13083-970 – Campinas – SP

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ABSTRACT

Preliminary results of the study of carbon nanotubes growth, using two different catalytic chemical vapor deposition techniques (plasma-enhanced low-pressure CVD and atmospheric-pressure thermal CVD) are presented. Nickel thin films were used as a catalyst material for the synthesis. Multi-walled nanotubes with diameters as small as 10 nm were successfully grown and analysed by high-resolution scanning electron microscopy.

1. INTRODUCTION

Carbon nanotubes (CNTs) attract a lot of attention since their discovery in 1991 [1] due to exceptional mechanical, electrical and optical properties. Numerous potential applications in nanoeletronics and nanofabrication include: electron field emitters, gas and energy storage, nano-transistors, scanning probe microscope tips, nanosensors, etc. [2,3].
For the CNTs growth, a number of methods was developed, including arc-discharge, laser ablation and different versions of catalytic chemical vapor deposition (CVD). As a catalyst for the carbon nanotubes growth by CVD, transition metals like Ni, Co, Fe and their mixtures with another metals (Al, W, Mo, etc.) are used. The growth occurs as a results of thermal decomposition of a carbon-containing gas (methane, acetylene, etc.) on the catalyst surface. Two possible growth modes (tip-growth or base-growth) are considered [2,3]. CVD techniques usually require elevated temperatures for the catalysis, but they have certain advantages over other tecniques as they provide a way for controlled, directional growth of both single-walled and multi-walled CNTs. For aligned CNTs fabrication, external eletric fields or template-confined growth can be used.
In the present work, first results of the CNTs synthesis study performed in the Center for Semiconductor Components - CCS (UNICAMP) using two different catalytic CVD techniques (plasma-enhanced low-pressure CVD and atmospheric-pressure thermal CVD) are presented. Multi-walled CNTs with tube diameters ranging from about ten to hundreds of nanometers were obtained and analysed using high-resolution scanning electron microscopy.

2. EXPERIMENTAL

In the present work, thin Ni films (1-50 nm thick) were used as a catalyst material. For the film growth, high-vacuum electron-beam thermal deposition was employed. As substrates, Si wafers were used, previously covered by thin (50 nm) thermally grown oxide films. The oxide film is necessary to avoid the catalyst diffusion into the Si substrate during high-temperature processing. After Ni deposition, the films were thermally treated (~700° C) in a nitrogen or hydrogen atmosphere to provide formation of separate catalyst nanoparticles/nanoislands.
CTNs synthesis was realized in two different reactors. The first one uses a microwave plasma source, with low-pressure (~1Torr) nitrogen-acetylene gas mixtures. Nitrogen is injected in the upper part of the reactor where plasma is created. The plasma flows down inside a quartz tube 50 cm long. The growth process occurs in the downstream region of the reactor where the sample is placed. Acetylene gas is injected near (above) the sample surface. Samples are heated up to ~500-700 ° C by a halogen lamp heater, located below the sample. The growth time was 10-20 minutes.
In the second reactor, the flowing gas mixture and samples are heated in a conventional resistive heating furnace to temperatures up to 950° C. Atmospheric pressure methane based mixtures with hydrogen or nitrogen were used. In this case, methane is employed as a carbon source as it decomposes at higher temperatures than acetylene. The growth time was 10-40 minutes.
In both reactors, the samples were treated by hydrogen or ammonia before the growth process for 5-10 minutes.
After synthesis, the samples were examined using high-resolution scanning electron microscopes (SEM) JSM-5900LV and JSM-6330F of the LME/LNLS, Campinas.

* stanisla@led.unicamp.br

3. RESULTS AND DISCUSSION

The first results obtained here (see Figs. 1-4) have shown that the CNT growth is possible in both reactors. The process appears to depend critically on the catalyst film thickness. For thicker Ni films, large diameter (in some cases, up to 100 nanometers or more), mostly randomly oriented, tangled tubes, apparently with high content of amorphous carbon were deposited. For thin catalyst films, it was possible to grow long (~1μm or longer), straight and small diameter (as small as ~10 nm) tubes, see Fig. 4.

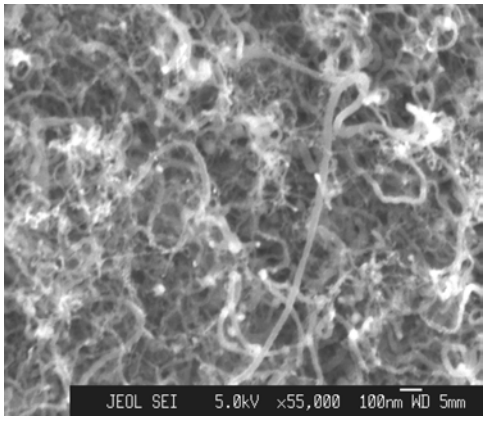

Figure 1 - SEM image of CNTs grown by low-pressure plasma-enhanced CVD, Ni film thickness of 6 nm, 550 ° C, growth time 10 min.

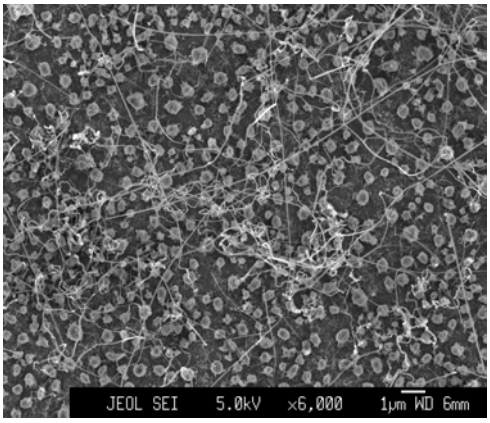

Figure 2 - SEM image of CNTs grown by atmospheric pressure thermal CVD, Ni film of 50 nm, 900 ° C, 20 min.

For thicker Ni films, larger and longer CNTs (growth rate up to 2 μm/min.) have been obtained. For higher growth temperature (atmospheric-pressure CVD), straighter CNTs can be obtained, especially for thinner Ni films.

In many cases, small bright catalyst particles were detected at the tip of the tubes, see Fig. 3. This suggests that the tip growth mechanism is likely to be responsible for the CNTs synthesis under the present conditions. In the same Figure, various defects and bamboo-like structures (diaphragms) inside CNTs can also be observed.

bamboo-like structures

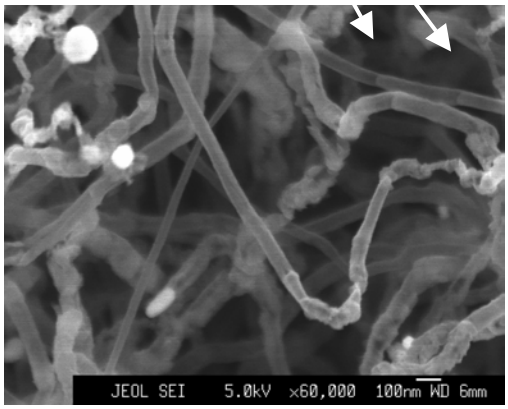

Figure 3 - SEM image of CNTs grown by atmospheric pressure thermal CVD, Ni film of 6 nm, 900 ° C, 20 min.

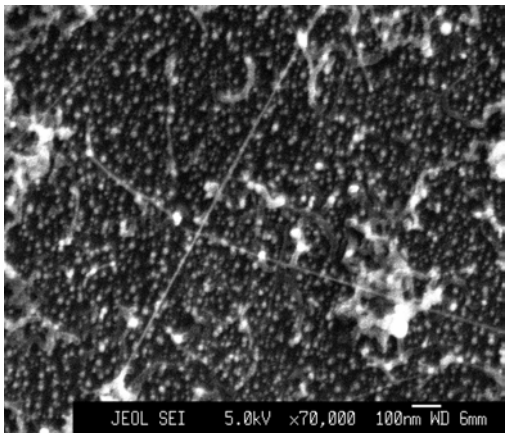

Figure 4 - SEM image of CNTs grown by atmospheric pressure thermal CVD, Ni film of 1 nm, 900 ° C, 20 min.

4. CONCLUSIONS

The presented results show that multi-walled CNTs growth with Ni catalyst is possible in both reactors (low-pressure plasma-enhanced CVD and atmospheric-pressure thermal CVD), apparently dominated by the tip-growth mechanism. The process appears to depend strongly on the catalyst film thickness and the process temperature. The future work will focus on the optimization of the growth processes, in particular, in order to achieve directional CNTs growth.

5. REFERENCES

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