

Carbon Nanotubes

The Challenges of the First Syntheses Trials

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Abstract: Carbon nanotubes (CNTs), due to their unique properties, are suitable for application in biomedical devices. However these devices are not available in the market because of problems associated with biocompatibility and synthesis reproducibility. Indeed, the production of vertically aligned-carbon nanotubes (VA-CNTs) is needed for most of these applications. The most common synthesis method, Chemical Vapor Deposition (CVD), involves a large number of parameters, not all known, and their influence on the process is not fully understood. Knowing that the synthesis of CNTs is performed in a variety of lab conditions and in different furnace systems, which makes it impossible to create a universal recipe for use in all labs, this paper aims to start the design of a universal protocol that all labs can use to generate a suitable recipe for their environmental conditions and furnace system. The influence of parameters such as best deposition spot and tube baking was assessed. During this evaluation, the importance of other factors (catalyst uniformity and climacteric conditions) to the process has been revealed. The universal protocol suggested is in an early stage and needs to be improved.

1 INTRODUCTION

Nowadays, carbon nanotubes (CNTs) are one of the most promising and exciting materials in nanomaterials research field, own to their unique electrical, mechanical and chemical properties. These properties make CNTs suitable for many biomedical applications (Raffa et al., 2011).

Indeed, CNTs found application in scaffolds for tissue engineering (Tran et al., 2009), namely for bone (Newman et al., 2013) and nervous tissue repair and regeneration (Fabbro et al., 2013). CNTs can also be used as drug and gene delivery devices (Tran et al., 2009).

There are several reports about electrochemistry biosensors for medical purposes that include CNTs on its electrodes (Jacobs et al., 2010). Biofuel cells work similarly to the enzymatic biosensors, so naturally CNTs were included in these devices (Holzinger et al., 2012). Others applications reported are neuronal electrode interfacing (Bareket-Keren and Hanein, 2012), microfluidic devices (Chen et al., 2012), carbon nanotubes-based X-rays devices

(Calderón-Colón et al., 2009) and flexible pressure sensors (Sepúlveda et al., 2011).

The list of applications of CNTs on the field of medical devices is vast but despite this growing research, CNTs still suffer from two main hurdles: i) the biocompatibility and ii) the synthesis reproducibility (the focus of this paper).

The majority of the listed devices require the incorporation of vertically aligned-carbon nanotubes (VA-CNTs). The most common synthesis process for the production of CNTs with this arrangement is Chemical Vapor Deposition (CVD). This process involves a large number of parameters and some of them may be still unknown. The ways that these parameters influence each other and the process are not completely understood (Oliver et al., 2013).

Furthermore, CVD process is many times performed in non-cleaning environments so the ambient conditions of each lab influences the synthesis as so the furnace system (Oliver et al., 2013). There are many different furnace systems and their geometry and function affect the process. So, these variations between labs prevent the

reproducibility of results.

Because of the differences in ambient conditions and in furnace systems between labs, it is not possible to make a general recipe that can be used in all labs, achieving the same results. Instead, one needs to create a universal protocol that can enable each lab to evaluate the influence of the parameters in its own environment, and create a recipe appropriate for its system.

This paper pretends to give an initial insight on how this protocol can be performed. For that the influence of the best deposition spot and tube baking were evaluated. During the evaluation of these parameters, others factors revealed to be important for the process such as the catalyst uniformity and the climacteric conditions.

2 CNT SYNTHESIS

There are several techniques to grow VA-CNTs, but the most common one among the different research groups is based on a modified CVD system. In a broad sense, in this technique, a carbon precursor in its gaseous form flows inside a tube at elevated temperature and enters in contact with a catalyst (Figure 1).

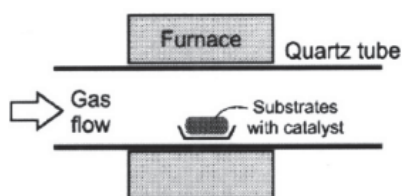


Figure 1: Furnace CVD system. Adapted from Hart, 2007.

Catalysts are used with two purposes: have an on-site pyrolysis of the precursor and support the CNTs during and after growth. The most important properties when selecting a material for catalyst are its ability to dissolve carbon at elevated temperatures, the carbon diffusion rate, the melting point and the equilibrium vapor pressure (Jourdain and Bichara, 2013). Among the most common catalysts, one can find Fe, Ni and Co, which are transition metals that reveal high solubility for carbon (Hart, 2007).

A thin-film of catalyst is deposited on a substrate where one desires to grow the CNTs. The most common one is silicon due to its compatibility with the catalysts and due to the melting point higher than the process temperature.

The CVD synthesis process requires the use of

three gases: the carbon precursor, a reducing gas and an inert one.

The precursor provides the carbon for the CNTs formation. This gas can be an hydrocarbon (Wang et al., 2014), an alcohol (Chen et al., 2014), an aromatic compound (Atiyah et al., 2011) or a natural carbon source (Qiao-juan et al., 2013).

The reducing gas, as the name implies, reduces the oxide that forms when the catalyst is not well stored. Also, it helps the formation of the catalyst nanoparticles and it keeps the catalytic sites active during all the growth process (Figure 2).

The inert gas is used during the process to control the pressure inside the tube if needed, and as a cleaning gas at the beginning and at the end of the synthesis process. Furthermore, it helps heat transfer during heating or cooling stages.

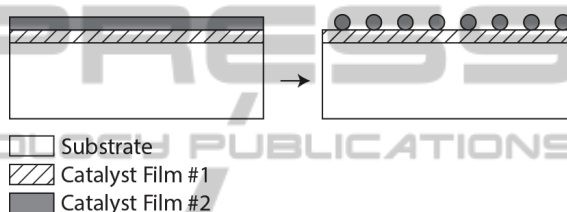


Figure 2: Formation of the catalyst nanoparticles by the action of hydrogen. Adapted from Hart 2007.

The CNT synthesis process can be divided into five stages (Figure 3): the cleaning, the dewetting, the growth, the delamination and the cooling.

The first stage consists on the cleaning of the lines, with the respective circulating gas, and of the tube with an inert gas.

The second one involves heating the tube to operating temperature and the catalyst reduction. In this stage there is also the formation of the catalyst nanoparticles, the dewetting step (Figure 2). The size of these nanoparticles is very important, because it will determine the diameter, the number of walls and the alignment of the CNTs (Jourdain and Bichara, 2013; Hart, 2007). The size can be controlled through the control of the temperature, flow and exposure time to the reducing gas. After this stage, the flow of the reducing gas is kept steady to maintain the catalytic sites active during the next step.

The third stage is the growth itself. The carbon precursor starts to flow in the tube and its degradation occurs by temperature and catalyst actions. The carbon resulting of these actions is adsorbed in the catalyst nanoparticles and precipitates when the particle is saturated, beginning the growth (Hart, 2007). The growth stops when the particle is encapsulated by amorphous carbon and

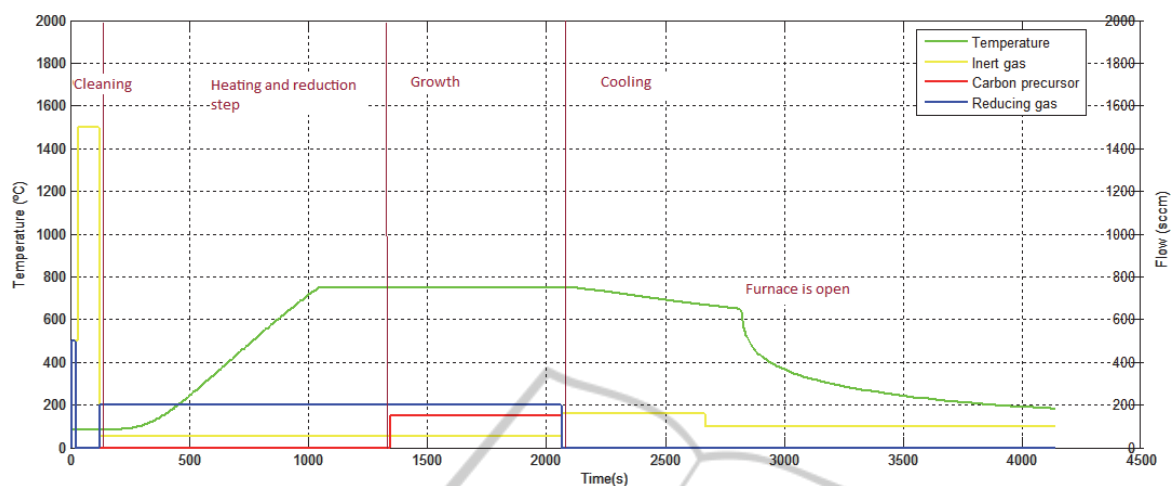


Figure 3: Steps of growth process.

other carbon compounds that form during this process (Brukh and Mitra, 2006).

The previous stages are the most important for the overall process. There can be an optional step, the delamination, which eases the removal of CNTs from the substrate.

The last stage is the cooling. Only the inert gas flows inside the tube to assist the heat transfer and to clean the gases and the wastes that remain in the tube. The CNTs can only be removed from the tube when the temperature cools down.

The equipment used for CNTs growth was a furnace Nabertherm, model RS 80/750/11, which is connected to three valves MKS Instruments, model RS-485, that control the gases flow. This setup is connected to a computer which controls the heating and cooling of the furnace as well as the flows.

The quartz tube used in this study had 25 mm of internal diameter and a length of 1000 mm. The selected gases were ethylene as the precursor gas, hydrogen as the reducing gas and helium.

Thin-films of alumina and iron, 10 and 1 nm thick respectively, were deposited via e-beam technique on top of the Si wafer as catalysts.

3 PROCESS PARAMETERS

From the previous section, one easily identifies a number of parameters that can be tuned to set the CNTs synthesis. Figure 3 illustrates a standard recipe for CNT growth via CVD technique.

3.1 Gases Flow/Time

Ethylene, hydrogen and helium are the gases used in

this study.

Helium is the inert gas with the main role of cleaning and assist the heat transfer inside the tube.

The ethylene is the carbon precursor. Its flow inside the tube is a key parameter. When selecting the flow, it must be taken into account that lower flows mean higher residence time and more probability of the reactions needed to form CNTs to occur, than if we had higher flows. However, at the other hand, it decreases the refresh rate of the gas inside the tube (Brukh and Mitra, 2006). Another aspect is the heights of CNTs forests increase with the growth time but not in a linear fashion. Indeed, from a certain time, forests are not higher because the catalyst nanoparticles are encapsulated in amorphous carbon, preventing them from degrading more ethylene and adsorb more carbon (Kumar and Ando, 2010).

The time and the flow of hydrogen influence the size of catalyst nanoparticles, which in turn influence the diameter, the number of walls and the alignment of CNTs (Jourdain and Bichara, 2013; Hart, 2007). In the growth step, this gas is essential for keeping the catalytic sites active.

3.2 Temperature

Temperature also affects the process as it is involved in the reduction process of the oxide and in the ethylene's pyrolysis.

It is important to understand the temperature profile inside the tube and to have it correlated to the length of the tube. In order to minimize the variation of the temperature inside the oven towards the tube endings, the furnace has isolation sleeves at the tube endings that not only ensure the tube centering

inside the oven cavity but also minimize the temperature loss towards the exterior.

Because the synthesis process is based on chemical reactions, one should not forget that there are thermal and chemical inertia associated with the reactions.

3.3 Silicon Pieces

The positioning of the pieces inside the tube also affects the growth process. The ethylene's degradation occurs driven by temperature and catalyst actions. There is thermal and chemical inertia, so the initial part of the tube is not the best place for the positioning of the pieces. As the gases enter in the tube at room temperature, it is necessary to consider the time required for the gas to achieve the required temperature. This requires time, which in a continuous flow, forces the pieces to be positioned towards the tube's downstream side.

However, as the ethylene travels along the tube undergoes air pyrolysis driven by temperature. The resulting compounds can be adsorbed on the catalyst nanoparticles to form CNTs or may continue to travel along the tube. If the latter is verified, they begin to recombine into more complex molecules that can contribute to the encapsulation of the catalyst nanoparticles, and consequently to the end of growth (Brukh and Mitra, 2006). This suggests that the closer the end of the tube pieces are placed, the lower the height of the CNT forests obtained.

The identification of the growth "sweet spot" in the tube is key to ensure a reproducible and consistent synthesis process.

3.4 Other

Tube baking is another parameter that affects the growth, but its influence is not well established. After a growth, there are a few residues that still remain in the tube. If they are left in the tube they may influence the next growth session. To minimize the impact of the debris, a tube baking is performed. To do so, the tube, while open, is raised up to 750 °C for 10 minutes. This process burns all the residues inside the tube, leaving it cleaned. This baking process can be seen as a strategy to reset the tube. Figure 4 shows the accumulation of debris after three growth sessions, as an example.

4 APPROACH/STRATEGY

This paper reports the study to identify the best

positioning inside the tube for CNTs' synthesis and the influence of tube baking during the process. These two parameters are standard to anyone who begins to synthesize CNTs in a laboratory.

For the realization of such study, a test protocol was established. In each working day, one would perform three growths and do a reset (bake) at the end of the day.

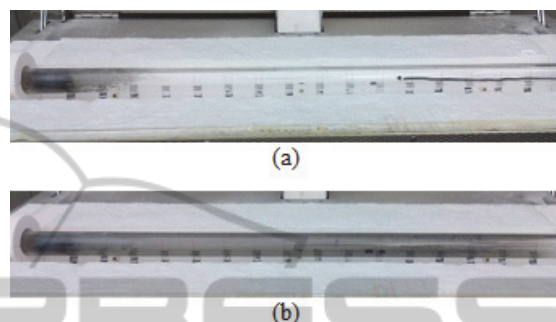


Figure 4: Aspect of the tube a) after the bake, b) after three growth sessions.

In each session, two pieces would be placed inside the tube. These pieces were cleaned with alcohol, acetone and nitrogen prior to their placement. The silicon pieces had all the same dimensions (10 mm x 10 mm) and were positioned with a distance of 10 mm between them. These pieces provide sufficient catalyst volume to trigger the local pyrolysis.

In order to start the study, it was necessary to set a starting recipe for the CNTs growth. The starting recipe consisted in a dewetting time of 5 min, with a flow of hydrogen of 200 sccm. At the same time, the tube was heated until its temperature reached 750 °C. The growth duration was of 12 min and the ethylene's flow in this stage was of 150 sccm. In the beginning of the recipe, the tube was cleaned with helium, which was also used at the end while the tube was cooling down. This recipe was based on literature review compilation and comparison (Stein and Wardle, 2013; Wardle et al., 2008; Garcia et al., 2008).

The height of the CNTs forests produced was measured using a magnifying glass of the brand LEICA, model M-80.

For the analysis of morphology of some samples and their chemical characterization, it was performed SEM analysis by a microscope Nova NanoSEM 200, FEI Company. This microscope has integrated an Energy Dispersive Spectrometer (EDS), which allows the chemical characterization of the samples by the analysis of its X-ray spectrum.

5 RESULTS AND DISCUSSION

The first parameter to be evaluated was position. Knowing that there is a certain degree of thermal and chemical inertia as said before, the pieces were positioned from the center of the tube (position 0 mm) towards the downstream in the direction of gases flow. The stopping criterion was the identification of a deflection point on the height's trends along the tube.

The main objective of the evaluation of this parameter was to identify the location within the tube where the CNTs obtain the greatest height and where the results show less variation.

Figure 5 shows the heights of the produced CNTs forests as a function of pieces position inside the tube, using the starting recipe.

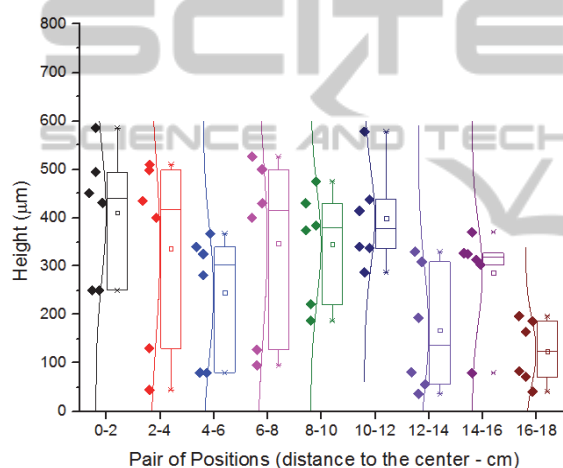


Figure 5: Height of the obtained CNTs forests in function of pairs of position of the pieces inside the tube.

Although Figure 5 shows some trend, one can argue that the variation of heights among the samples is large for the height average (Table 1). This non consistency growth led to the thought that it was not related to the growth parameters but instead to the catalyst deposition.

Table 1: Pairs samples' values for average and standard deviation.

Position	Height Average (µm)	Standard Deviation	Standard Deviation (%)
0-2	410	134.9	32.9
2-4	336	199.0	59.2
4-6	245	131.4	53.6
6-8	346	188.2	54.4
8-10	345	115.6	33.5
10-12	399	103.6	26.0
12-14	168	129.8	77.3
14-16	286	104.0	36.4
16-18	124	66.8	53.9

In order to sort the above issue, a new wafer with new catalysts films was requested from other supplier (INESC MN) that had fine control of the deposition process.

With the new samples, the growths were repeated for the positions 8-10 and 10-12 (Figure 6), the ones that were considered from the first set of growths to be the most relevant.

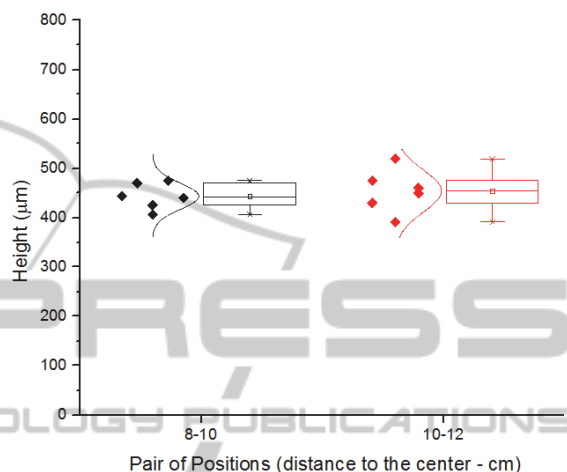


Figure 6: Height of the obtained CNTs in function of pairs of position of the pieces inside the tube for the case of the revised catalysts deposition.

As one can observe, the standard deviation was drastically reduced (Table 2), which confirms that the problem verified with the previous study was caused by the non-uniformity of catalyst deposition.

Since both pairs of position have low standard deviations and considering that the pair 10-12 has the highest height average, this pair was chosen as the best deposition spot for the current system.

Table 2: Pairs samples' values for average and standard deviation for the case of the revised catalysts deposition.

Position	Height Average (µm)	Standard Deviation	Standard Deviation (%)
8-10	443	26.3	5.9
10-12	454	43.1	9.5

Probably after position 12, phenomena of formation of complex molecules are occurring, consuming the precursor available and leading to the encapsulation of the catalyst nanoparticles, and consequently, to the reduction of the height of forests as seen in the Figure 5 graphic.

Since its entrance on the tube, the ethylene is suffering aerial pyrolysis. The resulting products (carbon and/or carbon compounds) can be adsorbed in the catalyst nanoparticles as well as ethylene which did not react. These compounds will undergo

catalyst pyrolysis. The results suggest that the contribution of the two types of pyrolysis is maximum in the pair of positions 10-12, reaching in this place the forests with higher heights.

Next, the influence of the tube baking in the forests' height was tested. Figure 7 shows the relative heights of three growth sessions realized during three days. Note that the higher heights obtained compared to the previous runs were due to the increase of the ethylene time to 25 minutes. This increase was performed in order to obtain tall forests for the analysis.

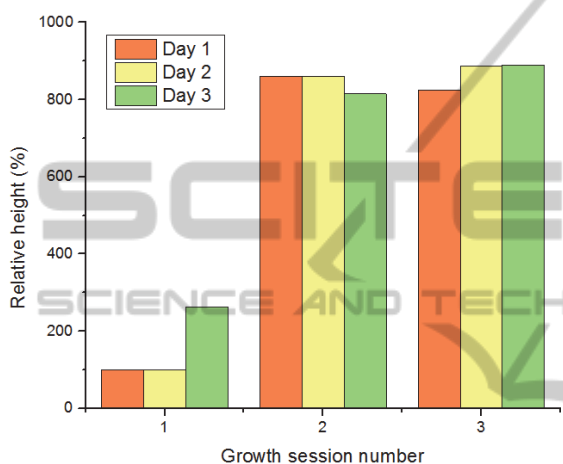


Figure 7: Height (in percentage in respect to the first growth of the first day) of CNTs in the 3 sessions performed during 3 days.

The first session of each day presents always the worst results. After this growth, the forests reach greater heights. These results suggest that the first session after cleaning the tube leaves some residues, which are essential for the next growths.

In order to further evaluate this, it was tested how long the tube could go in terms of growth sessions without performing the baking (Figure 8).

In the graphic of Figure 8 it is possible to see that after the fifth growth the heights of CNTs begin to decrease. Seeing that there is residues accumulation in the tube since the first growth, after 125 min of ethylene (cumulative time from all sessions), the amount of residues inside the tube becomes noticeable and starts to deposit on the top of the forests, preventing the precursor from reaching the catalyst nanoparticles.

Observing the SEM images (Figure 10a and Figure 10b), this color change seems to be caused not only by the deposition of carbon with a different structural arrangement, but also by the presence of other substances. The analysis of X-ray spectra in the regions indicated in Figure 10(c) and (d) was

performed to check if there are other substances present at the top of the forests. The results are shown in the Table 3.

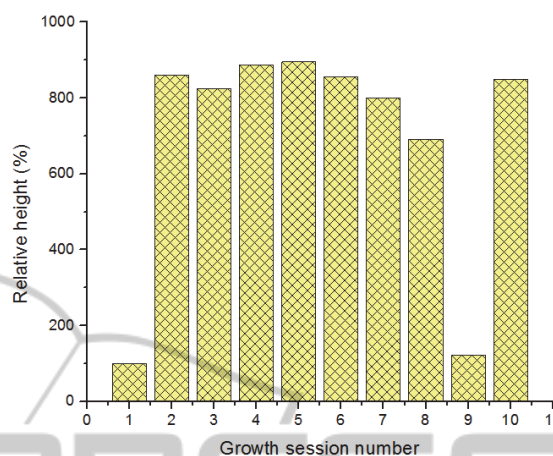


Figure 8: Height of CNTs, in percentage in respect to the first growth, during 10 sessions without cleaning the tube.

The deposition of debris was confirmed by observing a color change in the forests for a gray tone (Figure 9) and by the analysis of the X-ray spectrum held by SEM (Figure 10 and Table 3).

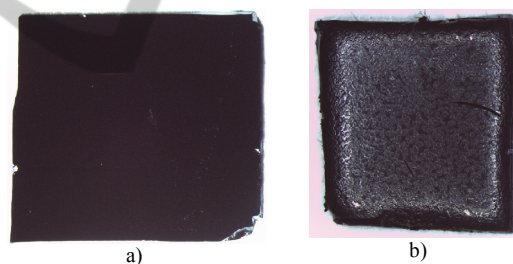


Figure 9: a) Piece with normal color, b) piece with gray tones.

Table 3: Results of the chemistry analysis performed on the regions Z1, Z2 e Z3 by the determination of the respective X-ray spectrum.

Region	Mass percentage (%)	
	Carbon	Oxygen
Z1	97.60	2.40
Z2	97.75	2.25
Z3	92.10	7.90

It was found that, in addition to carbon, there is also oxygen. This oxygen may result from the reduction step where the iron oxide is reduced to iron. In this step occurs the formation of hydroxides, which eventually settle on the top of the forests. Despite their different aspect, the regions Z1 and Z2 have similar chemical compositions, suggesting that the morphological differences between these two

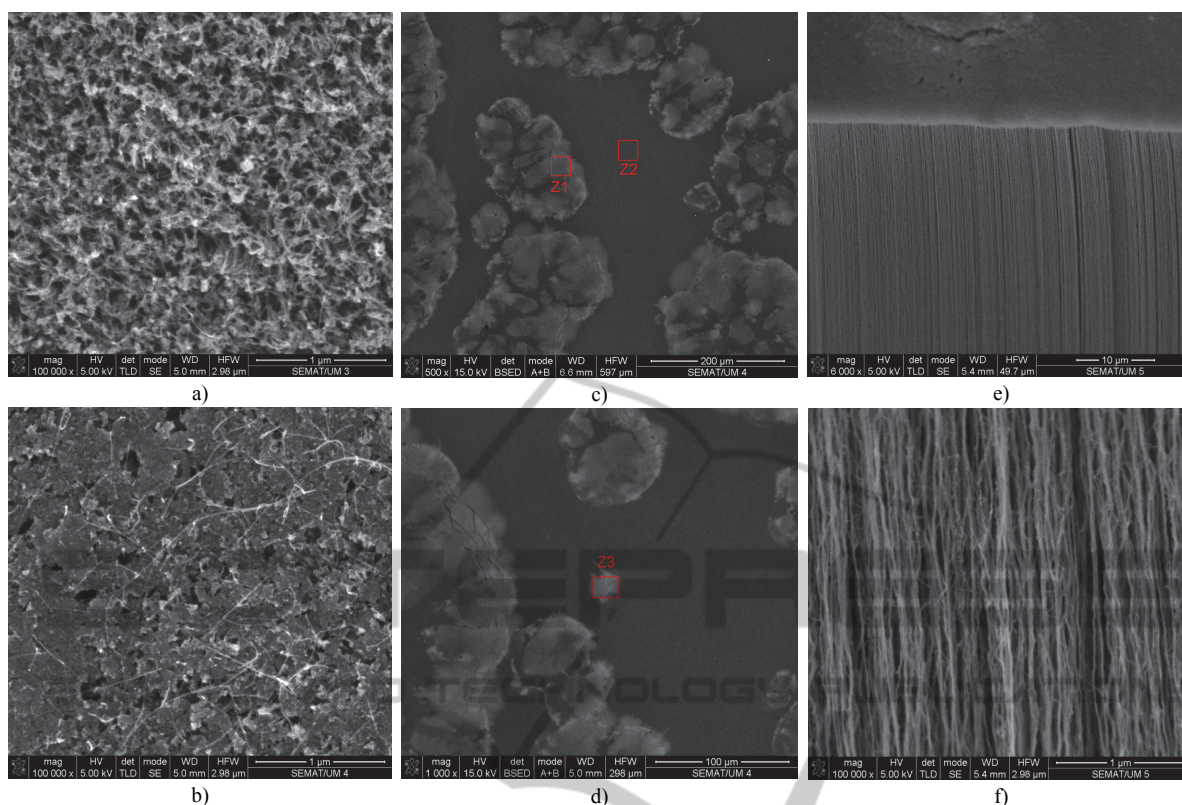


Figure 10: SEM images of the top view of CNTs forests after: (a) 5 sessions; (b) 7 sessions without performing tube baking. c) Regions Z1 e Z2 on the top of the forests where were performed X-ray spectrometry analysis. d) Region Z3 where was performed X-ray spectrometry analysis. e) and f) Lateral view of CNTs. It is possible to observe the: (e) the alignment; (f) the waving.

regions are due to carbon deposition with a different structural arrangement. So, the visible morphological changes are due to not only the presence of hydroxides but also to the deposition of carbon with a different structural arrangement.

Despite the effect on the top of the CNTs forest, a cross section view of the forests shows the vertical alignment (Figure 10e and Figure 10f).

6 CONCLUSIONS

From the results obtained in the parametric study is possible to start a universal protocol for generate the best recipe for each system and for each lab.

Throughout the analysis of the best deposition site, problems related with the non-uniformity of the catalyst film deposition were raised. These problems emphasize the importance of this key step. The deposition of the catalyst film must be of high quality in terms of uniformity and thickness to ensure, respectively, the uniformity of the forest itself and the CNTs alignment. The catalyst should

be protected of the environment, for example, by photoresist, to avoid its oxidation and the formation of undesirable substances during the synthesis that can affect the morphology and properties of the forests.

About the protocol itself, first one should established a starting recipe based on literature review and accordingly to the system characteristics. After that, the first parameter to be evaluated should the best deposition spot, taking into account the reactions that the precursor suffers since it enters the tube.

After finding the best deposition spot, the starting recipe should be adjusted to this position in terms of fluxes and growth time. Then, one should evaluate how far the system can go in terms of growth sessions without doing the baking. After controlling all these parameters, one should study the way in which the heights vary with the ethylene time. This step enables the control of the forest height in accordance.

This paper presents an initial approach on how to perform a parametric study.

More work has to be developed for answering some questions that have risen, namely at the room humidity and temperature level, which revealed some influence on the on the process but that was not able to be monitor at the time.

About the tube baking, there is the need to understand why, in this system, the residues left on the tube in the first growth are essential and improve the results in the next sessions and what residues are those. An approach to “see” inside the tube should be created in order to evaluate the substances remaining in the tube after the growths and how they behave to contribute to reducing the heights obtained.

The universal protocol proposed in this paper is only an initial model, which still needs to be improved by solving the raised questions and by enhancing the parametric study developed.

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