In-situ carbon nanotubes growth characterization during DC PE-CVD process

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CVD techniques are mostly used to produce CNTs films and in this method, modifications of growth parameters such as substrate temperature, catalyst or gas mixture are of great influence on growth. Then, depending on the growth protocol, structures with different morphology and properties can be obtained. For example, plasma enhanced CVD (PE-CVD) produce highly oriented CNTs films even in low density compared to thermal CVD. Moreover, as we will show DC PE-CVD allows for a simple *in-situ* growth characterization by measuring the plasma current. The relation between plasma current and growth mechanisms will then be shown and discussed.

Few nm thick Ni layers were sputter deposited on Si (100) to act as catalyst. Substrates were heated up to 1000°C under N_2 atmosphere. After few minutes, plasma was switched on with a potential of about 400 V. CH_4 was then introduced into the chamber (t=0'). Figure 1.a shows SEM pictures of the initial Ni layer, after heating and after 5, 10, 30 and 45 minutes of plasma. Clustering takes place during heating and CNTs only appear after 5 minutes of plasma. Figure 1.b represents the evolution of CNTs geometric parameters (length, density, diameter and orientation) with plasma process duration. Two different regions appear in these curves: in region 1, clusters are modified (density and diameter) and CNTs growth takes place in region 2. Plasma current versus time curve (I-t) is reported in figure 1.c. The I-t curve shows an evolution which can be correlated with the two stages observed by SEM. First, in region 1, plasma current sharply increase with time and in region 2 the evolution is linear.

Three growth steps will be used to understand these curves:

- Ni clustering.
- Ni carbide formation: carbon reactions on nickel whichmodify surface properties such as secondary electron yield. These variations induce a sharp increase of the plasma current. Then, in region 1 of I-t curves, we will characterize the nickel-carbide formation.
- CNT formation: if we consider CNT layer as a distribution of cylinders which growth linearly with time, cathode surface and therefore plasma current increase linearly with time. Moreover, the slope is dependent on the growth protocol (gas mixture, temperature, pressure, and plasma power…). The linear part of I-t curve will then be linked to the CNTs growth rate.

Both regions in the I-t curves can be related to important steps which are catalyst cluster activation and CNT growth. Therefore, in the case of CNTs growth, the plasma current is a good parameter to *in-situ* characterize DC PE-CVD. The influence of different parameters on CNTs growth will then be shown and discussed.

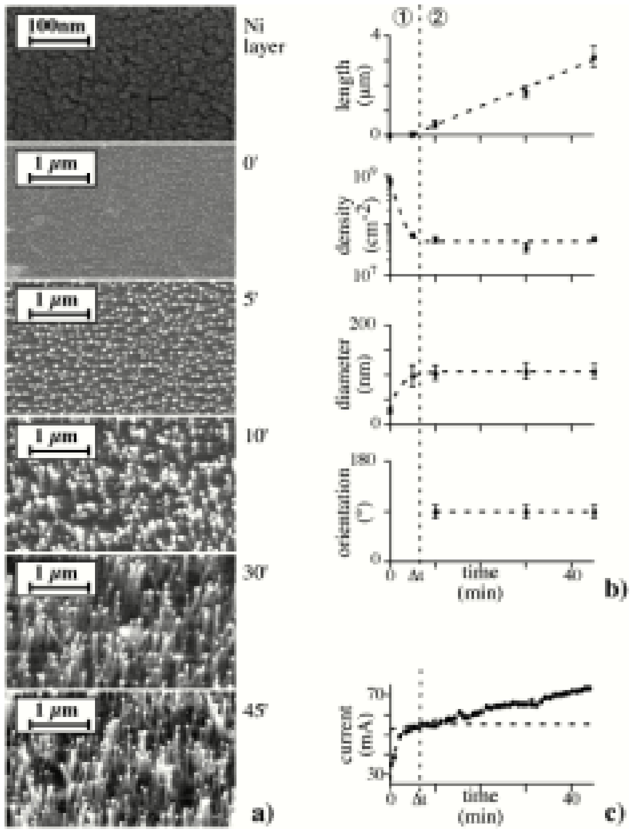

Fig. 1: a) SEM pictures at different growth time. b) CNTs geometric parameters evolution with time. c) DC-plasma current variation during growth.