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1 Introduction Single- and Multi-Wall Carbon Nanotubes (SWCNTs and MWCNTs) are materials of potential interest for a variety of applications thanks to their very high aspect ratio, their excellent electrical, thermal and mechanical properties, as well as their high chemical stability [1]. Carbon nanotubes (CNTs) can be fabricated using several different processes, as reviewed in [2]. Here we focus on a particular chemical vapor deposition method (CVD) assisted by localized laser heating. More specifically, we use a near-infrared laser diode to locally promote the growth of CNTs on a substrate having catalysts deposited on it.

The main issue with conventional CVD processes is the need for relatively high temperature (typically above 600 ºC) [2] that dramatically limits the type of substrates suitable for CNTs growth. A substrate having additional functional features, devices or components on it would suffer from high-temperature exposure. The rationale for our laser-based approach is to keep the heat localized enough so that most of the substrate remains at low temperature. With this scheme, heat sensitive features within the substrate are preserved. Further, the laser assisted approach offers additional flexibility as CNTs can be grown in predefined locations without the need for pre-patterning process. Laser assisted CVD methods are known methods for the preparation of different structures like fibers, thin films, microcoils, etc. out of different materials (B, BN, Si, W, etc.) [3] as well as carbon fibers ([4, 5]). Recently, MWCNTs [6-8] and SWCNTs [9-11] grown using Laser Activated Catalytic CVD (LA-CCVD) method were reported.

In this work, we report for the first time the production of vertically aligned forest of CNTs containing SWCNTs using the LA-CCVD method.

2 Experiments Our LA-CCVD process takes place in a small stainless steel reactor with a volume of 3.4 liters. The reactor contains the gas inlet and outlet, temperature and pressure sensors, two windows for in situ optical observation, a horizontal substrate holder and an optical assembly that focuses the laser beam on the substrate at a 35 deg incidence angle.

The specimens used are silicon substrates (0.5 mm) on which a 20 nm-thick Al_2O_3 layer is deposited. A 2 nm

thick Fe layer was sputtered on top. The specimens were mounted horizontally on a fused silica holder. The chamber was pumped down to approximately 10^{-3} mbar and subsequently filled up with a mixture of argon, hydrogen, and ethylene (in a ratio 8:2:5) until the chamber reaches ambient pressure. The substrate was then exposed to a continuous laser beam (Unique-mode AG, maximal power ~35 W) emitting at 800 nm. Laser beam intensity and spot size can be tuned giving the possibility to grow areas of CNTs with different sizes. Here, the spot size was about 100 µm and the irradiance 2.2×10^5 W/cm^2.

Raman spectroscopy and scanning electron microscopy (SEM) were used to characterize the growth products. Raman spectra were measured by a Jobin Yvon-LabRam spectrometer utilizing the 633 nm excitation wavelength and equipped with a microscope, which allows lateral resolution better than 2 µm. SEM images were obtained with a field emission gun environmental XL 30 ESEM-FEG Philips scanning electron microscope.

In this work, we investigate the effect of the laser exposure time on the presence of CNTs. To fulfill this objective, we made several experiments with increasing exposure time starting from 5 s up to several minutes. We identified three growth regimes that we describe in more details in the next section.

3 Results and discussion

3.1 Irradiation time ≤ 9 s No CNT Raman signal was observed suggesting the absence of CNTs. At the laser spot, the smooth surface of the iron film was transformed into an assembly of clusters with islands-like structure as shown in Fig. 1. The observed clusters have a broad distribution of sizes; from at least below 2 nm (spatial resolution of the SEM) up to around 55 nm. Clusters larger then ~3 nm are usually not active for SWCNTs formation but can promote the growth of MWCNTs or carbon fibers [2]. The temperature measured at ~1.2 mm distance from the laser spot increased with time and reached maximal value 245 ºC.

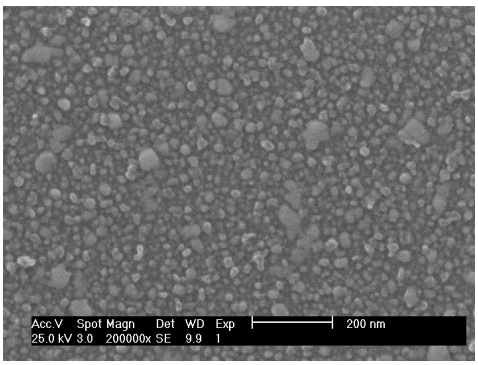
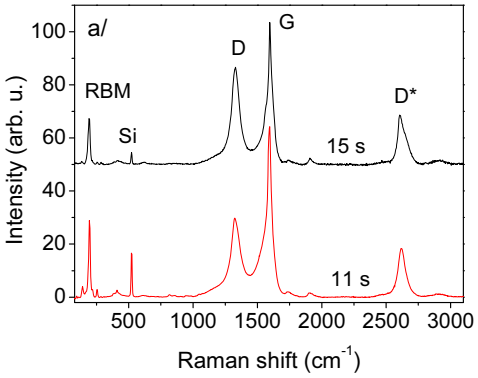


Figure 1 SEM image of the center of an area where the laser beam hits the specimen for 5 s. The surface structure changed but no CNTs were detected.

3.2 Irradiation time 11 s–15 s The Raman spectra obtained in the spot centers are shown in Fig. 2a for 11 s and 15 s of irradiation time. In both cases features typical for Raman spectra of SWCNTs [12] can be recognized; so called Radial Breathing Modes (RBMs), split G mode and D* mode were found. The intensity of the Si peaks at 303 and 522 cm^{-1} decreases with increasing irradiation time.



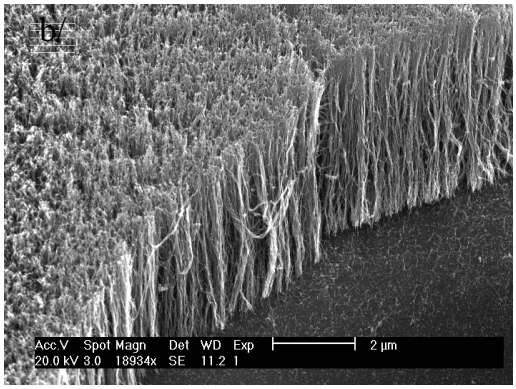


Figure 2 a) Raman spectra obtained in the center of the laser spots after 11 s and 15 s of irradiation, respectively. b) SEM image of a vertically aligned forest of CNTs after 15 s of irradiation.

This decrease corresponds to higher shielding effect of the thicker carbon carpet obtained for the longer irradiation time. The thickness of the vertically aligned forest of CNTs that is close to the center of the spot is about 3 µm after 15 s of irradiation as shown in Fig. 2b. The carpet's thickness decreases from the center to the periphery of the spot. The ratio of the Raman intensities of the Si substrate (522 cm^{-1}) and G mode illustrates the carbon carpet thickness dependence on the distance from the spot center. The thickness dependence has a Gaussian profile as shown in Fig. 3a (laser exposition time was 14 s). Figure 3b shows the RBM part of the Raman spectra obtained at different distances from the spot center. SWCNTs with different diameters were grown as seen from the frequency of the RBM modes. The distribution of SWCNT diameters spans from 1.8 to 0.9 nm at the spot center and from 1.3 to 0.7 nm in the spot periphery. Figure 3c shows the Raman shift

of the most pronounced RBM mode, localized at around 195 cm^{-1}. The SWCNT diameter decreases from 1.27 to 1.24 nm measured at the center of the laser spot and at the distance 133 μm away from it, respectively. No RBM mode was obtained when the distance from the center of spot is larger than ~150 μm in this case. Both, the shift of diameter distributions and shift of most pronounced peak can be explain with temperature dependent evolution of catalyst-cluster size. The mobility of existing metal clusters increases with increasing temperature and consequently the size of final clusters, suitable for CNTs nucleation, increases, as smaller ones agglomerates. Because of the temperature distribution across of laser spot (the temperature distribution results from the Gaussian profile of laser beam intensity), the probability of a forming of larger catalyst agglomerates is higher in the center of spot. Because the CNT's diameter is directly proportional to the size of the catalysts [2], larger SWCNTs (smaller RBM Raman shift) are consequently observed in the spot center. Temperature decreases with distance from the laser spot. It reached 266 ºC at distance ~1.2 mm after 15s of irradiation.

3.3 Long irradiation time (3 min) The growth of a carbon whisker at the hottest point of the substrate surrounded by a carpet of aligned CNTs was observed for exposure time of 3 minutes. The SEM images of the spot area and the area ~0.8 mm away from the spot are shown in Figs. 4a and b, respectively. Figure 4c shows a detail image of a vertically aligned forest of CNTs. The carbon

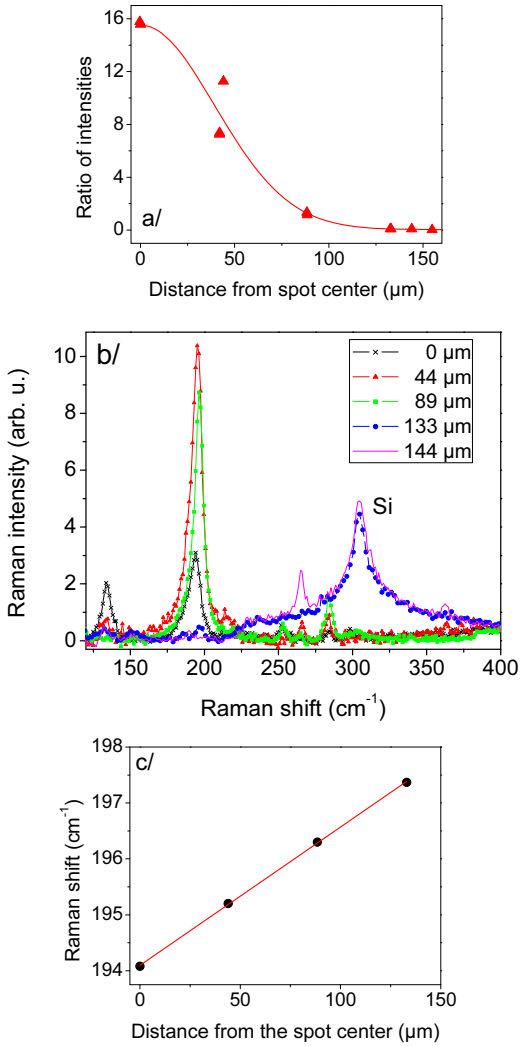


Figure 3 Data obtained on the spot after 14 s irradiation time. a) The ratio of Raman intensities of the G mode and Si mode (522 cm^{-1}) reflecting the carbon deposit thickness. b) Raman spectra obtained at different positions in the spot. Numbers indicate the distance from the spot center. c) The RBM mode (localized at around 195 cm^{-1}) shift measured across the spot.

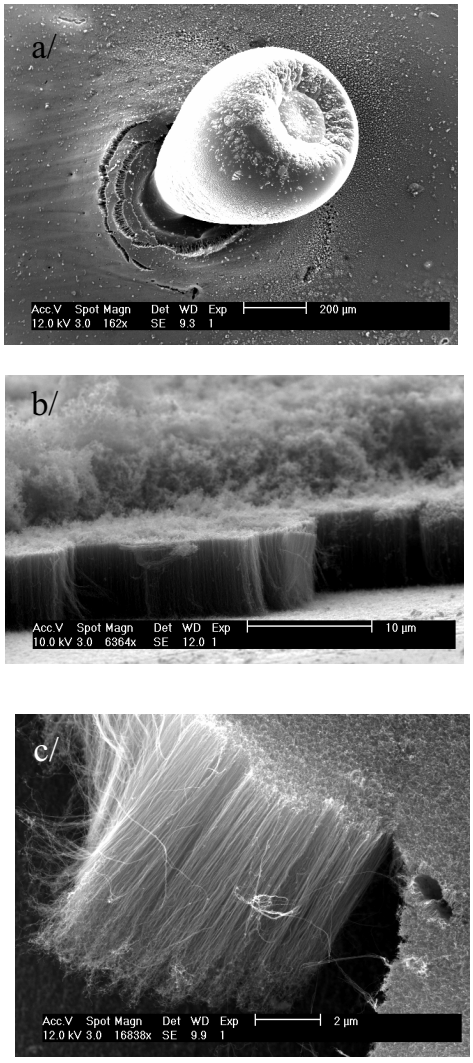


Figure 4 SEM images of a) carbon whisker deposit on the laser spot, b) vertically aligned MWCNTs covered by an amorphous carbon deposit, c) detailed picture of the vertically aligned forest of MWCNTs.

whisker (Fig. 4a) has a baseball bat shape with a height of about 0.7 mm and a maximum diameter larger than the diameter of the laser spot. The Raman spectrum measured on the whisker is shown in Fig. 5a. There are two important features - the spectrum is dominated by the D mode at 1337 cm^{-1} and there is no visible D* mode at about twice the D-mode frequency. Additionally, the D mode is larger than the G mode. These features are typical for amorphous carbon deposits. The surroundings of the whisker contain a carpet of vertically oriented, up to ~ 7 µm long MWCNTs covered by a layer of amorphous carbon. The SEM image shown in Fig. 4b was taken at the edge of a post-processing scratch that was made to reveal the CNT forest. The substrate, layer of the vertically aligned CNT carpet and the carbon amorphous layer are clearly visible on the image from bottom to top, respectively. The amorphous layer has the largest thickness close to the whisker. Figure 5b shows the Raman spectrum measured from the carpet ~0.8 mm away from the C-whisker. The spectrum is characteristic of a mixture of MWCNTs and amorphous carbon having D, G and D* modes.

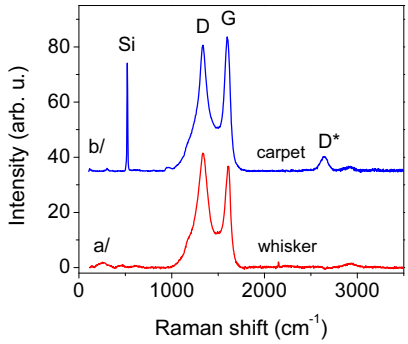


Figure 5 Raman spectra of a) the whisker and b) the carpet, both shown in Fig. 4.

It is known that the CCVD process of CNTs production consists of two basic steps, an activation of catalysts and a CNT growth process, respectively. Usually, during the activation process, the specimen temperature increases, the metal based layer is restructuring and metal oxides are reduced with hydrogen. Metal clusters that are formed can eventually migrate on the support layer and agglomerate. This metal clusters serve as catalysts for dissociation of a carbon rich gas and nanotubes nucleation and growth. In our case, the catalyst activation process occurs during the irradiation time < 9 s (no CNTs were observed), followed by the CNT growth at laser spot. For longer irradiation times, CNTs are formed around the spot as the temperature of the spot surroundings increases with time. In the case shown in Fig. 4, MWCNTs were formed outside of the laser spot. As the thickness of the carbon carpet on the laser spot increases, its temperature increases (for the laser line used carbon has higher absorption coefficient than the substrate) beyond the threshold temperature for thermal dissociation of C_2H_4, and amorphous carbon is deposited on CNTs.

4 Conclusion In this paper, we investigated the effect of laser irradiation time on CNTs growth. The experiments were performed on flat $Fe/Al_2O_3/Si$ specimens with 2 nm/20 nm/0.5 mm layer thicknesses in a cold wall reactor at ambient pressure of an ethylene-hydrogen-argon atmosphere with a ratio 5:2:8, utilizing a 800 nm wavelength laser.

At this point, we can identify three regimes during the laser activated growth:

- *Regime 1 (irradiation time < 9 s): Activation of catalyst.* The temperature at the laser spot was high enough to break the catalyst film into islands-like structure. No CNTs are observed in this regime

- *Regime 2 (11 s ≤ irradiation time ≤ 15 s): CNTs growth*. SWCNTs grow and form vertically aligned forest-like structures at the laser spot area where the temperature is sufficiently high.

- *Regime 3 (irradiation around 3 min): Overheating*. Whisker-like structure of amorphous carbon and vertically aligned forest of MWCNTs are grown both at the beam spot and around. An amorphous carbon deposit partially covers the CNT carpet because temperature increases beyond the threshold temperature for thermal dissociation of C_2H_4.

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