Laser-assisted growth of carbon nanotubes on laser-patterned substrates and inside sealed micro-channels

Y. van de Burgt\textsuperscript{a,b}, Y. Bellouard\textsuperscript{a}
\textsuperscript{a}Department of Mechanical Engineering, Eindhoven University Technology, Den Dolech 2, Eindhoven, The Netherlands; \textsuperscript{b}Holst Centre / TNO – Netherlands Organization for Applied Scientific Research, HTC31, Eindhoven, The Netherlands.

ABSTRACT

Carbon nanotube assemblies can be used for specific applications such as sensors and filters. We present a method and proof-of-concept to directly grow vertically-aligned carbon nanotube structures within sealed enclosures by means of a feedback-controlled laser-assisted chemical vapor deposition technique. The process is compatible with a variety of micro-fabrication processes and bypasses the need for post-process packaging. To further investigate the possibilities of small CNT structures we present a femtosecond laser patterning method. This laser is used to pattern either the catalyst before CNT growth, modifying the surface and catalytic conditions, or the CNT structures directly after growth.

Keywords: Carbon nanotubes, laser-assisted CVD, micro-channel, femtosecond laser, patterning.

1. INTRODUCTION

Owing to their special geometrical, structural and electrical properties, carbon nanotubes (CNTs) have been found to be useful in applications such as sensors\cite{1} and filters\cite{2,3} among many others. Their organic nature also allows them to be used in micro-fluidic biological applications and makes them compatible with many materials commonly used in micro-fluidics, such as PDMS or glass. For instance, vertically aligned carbon nanotube embedded structures have been proposed for enhanced particle interception in cell separation\cite{4,5} and as blood pressure sensors \cite{6}.

These applications use lithography in combination with thermal chemical vapor deposition (CVD) to control the geometry of the nanotube structure and embed the nanotubes inside the device by creating the micro-channel on top of the nanotubes. More convenient would be to directly grow the nanotubes inside the micro-channel without the need of an extra structuring or transfer step. Various techniques for local growth of carbon nanotube structures such as micro-resistive heating\cite{7} or micro-induction\cite{8} have been proposed. Although these techniques provide the possibility of localized heating and CNTs growth, it has intrinsically limited flexibility.

In this paper, we present a laser-assisted fabrication method for local \textit{in-situ} growth of carbon nanotube structures inside enclosures.\cite{9} This technique eliminates the lithography structuring step and increases the versatility of the process since a laser-beam can be used virtually anywhere in the channel. Specifically, as a proof-of-principle, we show the growth of a hill of vertically aligned carbon nanotubes inside a micro-channel created by femtosecond laser processing.

Furthermore, we also demonstrate the possibility of using a femtosecond laser to pattern the surface of the substrate, before or after CNT growth. In this way smaller CNT structures could be created as well as a possible better diameter size distribution by a more discrete catalyst nano-particle size production.

2. EXPERIMENTAL

Carbon nanotube chemical vapor deposition (CVD) growth consists of a thermal energy supply, a catalyst and a carbon-containing precursor gas. This growth method provides a high degree of control making it the most promising method for carbon nanotube growth.

Among CVD processes, laser-assisted ones differ from conventional CVD by using a laser to provide the thermal energy. This opens up new possibilities for direct-write growth as well as fast and local heating, enabling the growth site to be surrounded by temperature-sensitive elements and/or materials. Indeed, the laser-assisted CVD growth method is
compatible with most polymers and other materials or adhesives used in micro-fluidics. Inherent to the use of local heating is the non-uniform temperature distribution. Laser heating can also induce some possible overheating due to the dynamically varying absorptivity of the substrate during the CNTs growth process [10]. To bypass these issues, we use a temperature closed-loop controlled laser-assisted CVD process using emitted thermal radiation from the laser spot as feedback (a schematic of this setup is presented in Fig 1). Further control of the process is achieved by monitoring a photodetector signal measuring the variation of intensity of the reflected laser light from the growth site. This closed-loop control process is described in more detail elsewhere [11,12].

The femtosecond laser patterns are produced with a ytterbium-fiber based laser (1030 nm) with pulse duration of approximately 350 fs; a repetition rate of 400 kHz and an average power of maximum 220 mW, yielding a pulse energy of 550 nJ/pulse. The writing speed is set to 500 µm/s. The laser is focused by a 20x objective lens (NA = 0.4) to a spot with a diameter of 2 µm.

2.1 Growth inside micro-channel

In this experiment, the micro-channel is fabricated in a 500 µm-thick fused-silica glass slide with lateral dimensions similar to the substrate, 4 x 4 mm on which it stands. A femtosecond laser process was combined with etching for 24 hours in 2.5% hydrogen-fluoride (HF) solution to create the channel [13]. The open channel is 1 mm wide, 120 µm in height and has a length of 4 mm. For aligned carbon nanotube growth we use a silicon substrate covered with a 20 nm Al₂O₃ and a 1.5 nm iron catalyst layer both deposited by electron-beam evaporation. The laser used is a continuous-wave (CW) diode laser operating at a wavelength of 808 nm, focused to a spot of about 500 µm. To visualize and analyze the resulting CNT structures grown inside the channel by scanning electron microscopy (SEM), the channel was not permanently attached to the substrate. However, to show the proof-of-concept, Epotek 355nd epoxy is used to glue the two parts together at the side-edges of the substrate, so that the material combination can withstand the elevated temperatures around the laser hot spot. Other bonding processes such as anodic bonding could also be considered and are assumed to be more stable for the high temperatures involved here.

In Fig 2(a) a schematic of the channel growth is presented. The laser beam is focused onto the substrate through the fused silica channel, which is transparent to the wavelength of the laser, 808 nm. The channel itself only has two openings where the gas flows through.
2.2 Patterning

The pre- and post-patterning experimental procedure is as follows. In the case of pre-patterning (Fig 3(a)), the substrate containing only the catalyst is placed under the femtosecond laser setup. The post-patterning process is generally the same, only the femtosecond laser is focused on the CNT hill, as shown in Fig 3(b). The inset of the figure shows the specific pattern that is created in all the experiments.

Fig 3. Femto second laser patterning. (a) pre-patterning on a substrate containing only the catalyst. (b) post-patterning previously grown CNT forest. The circular inset shows the pattern used in the experiments.

3. RESULTS AND DISCUSSION

3.1 Growth inside micro-channel

Using the diode laser focused through the fused silica created micro-channel we could directly grow aligned CNT structures in the channel.

The proof-of-concept is presented in Fig 4(a) with a photo of the locally grown CNT structure inside the attached micro-channel. In Fig 4(b) a photo of the transparent micro-channel attached to the substrate is shown with the inset showing the (infrared) light emission from inside the channel during growth.
In Fig 5 corresponding scanning electron micrographs of the resulting growth are presented. This particular nanotube structure was grown in 150 sec and has an estimated height of about 100 µm. The lateral dimensions of the structure are about 800 x 600 µm. An overview of the substrate with corresponding CNT growth is shown in Fig 5(a). In Fig 5(b) a view of the side of the hill is given, from which the height was estimated. The insets show the Raman intensity signals for two positions on the sample. The ratio of D- and G-band intensities of the Raman signal can be used to evaluate the quality of the CNTs. Here, both signals indicate multi-walled CNTs, predicting the presence of a vertically aligned forest of multi-wall carbon nanotubes. In Fig 5(c) and Fig 5(d) detailed zooms of the aligned nanotubes are given. These pictures were obtained after scratching the nanotubes grown layer from the side in the direction of the gas flow. Fig 5(c) shows a zoom of the left side of the hill while the Fig 5(d) shows an enhanced zoom of the right side of the hill, visible by the slopes of the top of the nanotubes in both pictures.
3.2 Patternning the catalyst

In the previous section, we have demonstrated the use of a femtosecond laser to create a micro-channel in fused silica. Another possibility is to use this laser to pattern the surface of the substrate. Interestingly this can be done both before CNT growth as well as after.

If the substrate with catalyst is patterned with the femtosecond laser before growth the iron catalyst layer is modified so that it will directly influence the resulting growth. Ideally, the short pulses ensure the iron(oxide) catalyst layer to break up into small nanoparticles on which the CNTs can grow.

To demonstrate the influence of laser-fluence, we show CNT growth results for several laser pulse energies. Fig 6 shows the CNT growth result after femtosecond laser patterning for 104 J/mm² (53.2 mW) and 174.3 J/mm² (89 mW). It is clear that the growth during the low power, 104 J/mm² Fig 6(a) is not really influenced by the patterning of the catalyst. Interestingly though, the top of the CNT hill, still shows the pattern of the catalyst beneath, so apparently the catalyst and consequently the CNTs are indeed modified. This is more clear in Fig 6(b). In this figure, a zoom of the center of the CNT forest is visible. Clearly visible are the aligned CNTs as well as the pattern that was created by the femtosecond laser irradiation. In this case the catalyst is modified as such that it does not allow CNT growth taking place anymore. This could be the result of the catalyst layer transformed into larger particles on which CNTs cannot nucleate.

This effect becomes even more noticeable if we increase the power even further. In Fig 7, the catalyst is irradiated with a laser power of 103 and 203 mW respectively. In Fig 7(a) and (b) it is clear that the surface and catalyst layer are modified so that no CNTs could grow from it. In Fig 7(b), which is a zoom of the center part Fig 7(a), nano-ripples are visible. This figure also shows that no growth took place at the damaged surface. A number of nanotubes are still visible but they are believed to originate from the un-modified surface.

For the experiment in Fig 7(c), the power is even further increased. In this case it seems the femtosecond laser irradiation surface actually increased the CNT growth. In the center no growth took place but the circular region clearly shows more material then the direct surroundings. After Raman spectroscopy investigation we learned that the material produced here is probably not CNTs but some form of amorphous carbon with a high defect ratio.

From these results we can conclude that the femtosecond laser power should be less than 174.3 J/mm² to ensure CNTs can still grow on the catalyst surface. A structural quality measurement by Raman spectroscopy on larger modified surfaces should determine whether smaller and higher quality CNTs can be grown by tailoring the laser parameters.
Fig 7. SEM pictures of CNT growth after patterning of the catalyst by femtosecond laser exposure (a) 201.7 J/mm² (103 mW) (b) 398 J/mm² (203 mW). (c) Zoom of the straight part of the structure in (a). The surface shows nano-ripples and no originated CNTs.

3.3 Patterning CNTs post-growth

Using previously grown aligned forest of CNTs we could also investigate the influence of femtosecond laser exposing on the CNTs. A number is SEM pictures are shown in Fig 8 and Fig 9.

In Fig 8 we have investigated the influence of femtosecond laser irradiation of 104 J/mm² (53.2 mW) on an existing CNT forest. The pattern is clearly visible and Fig 8(b) shows that not all CNT are removed. A seemingly uniform layer of CNTs is still present. This demonstrates the ability to selectively remove a particular thickness of CNTs.

Fig 8. SEM pictures of CNT forests patterned by femtosecond laser irradiation of 104 J/mm² (53.2 mW) (a) Top view of structure modified by femtosecond laser. (b) Zoom of pattern that shows still nanotubes remain on the bottom of the structure.

The laser power for the experiment shown in Fig 9 has been increased to 398 J/mm². From this figure we can clearly see that the complete CNT layer has been removed. In Fig 9(b) a detailed zoom of one of the walls is shown and this shows the ability to created almost vertical walls inside aligned CNT forests. This figure also seems to show a thermally modified top layer of CNTs with some amorphous carbon re-deposition. A next step would be to see what the pitch can be between subsequent lines of femtosecond laser patterning. In other words, how small the resulting CNT features can be.
4. CONCLUSION

We have presented a laser-assisted closed-loop controlled carbon nanotube growth process that has the capability of growing locally aligned carbon nanotube structures inside a sealed micro-channel. As a result of the local heating the process is compatible with a variety of packaging technologies that may use adhesive, polymers or other temperature sensitive material.

The use of a laser makes the process versatile, enabling the growth of nanotubes at arbitrary positions within enclosure such as a micro-channel as demonstrated here. In addition, laser-assisted growth also opens up possibilities of scanning the laser within a cavity giving the possibility to create arbitrary patterns in an enclosure. For instance, this could be useful for lab-on-a-chip applications for creating filters[3].

To add even more flexibility to the process by removing the requirement of a deposited nanolayer, the catalyst could also be part of the gas feed, for instance using iron pentacarbonyl gas, Fe(CO)₅. In addition, to get absorption within a fluidic channel made of a transparent material, a non-linear absorption process such as multi-photons could be used. For instance, using femtosecond laser exposure of silica in the cumulative regime produces localized heat affected zones.[14]

In this paper, we have demonstrated another technique for preparing locally grown CNT structures for application purposes. By using the same femtosecond laser, we were able to pattern the CNT pre- and post-growth. Preliminary results show the influence of the laser power, enabling tuning to specific properties. A next step would be to investigate the influence of different and lower laser powers for pre-patterning of the catalyst and different repetition rate and writing speed.

REFERENCES


