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Laser-assisted growth of carbon nanotubes—A review

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Laser-assisted chemical vapor deposition (LACVD) is an attractive maskless process for growing locally carbon nanotubes at selected places on substrates that may contain temperature-sensitive components. This review gives a comprehensive overview of the reported research with respect to laser assisted CVD for the growth of carbon nanotubes. The advantages and disadvantages of local growth using laser sources are discussed, with a focus on structural quality and properties, such as length, position and alignment, and process control. The paper is divided into two parts. The first part deals with the influence that the main parameters for nanotube growth—gas, catalyst and thermal energy—have on the growth of carbon nanotubes by laser-assisted synthesis. The second part deals with the attempts and successes to control different aspects of local nanotube growth using a laser-assisted growth method. © 2014 Laser Institute of America. [<http://dx.doi.org/10.2351/1.4869257>]

Key words: carbon nanotubes, laser-assisted chemical vapor deposition, laser, direct write, localized growth, control, carbon nanotube applications

I. INTRODUCTION

Carbon nanotubes (CNTs) have attracted a lot of interest since the high impact publication in 1991 by Iijima.¹ Their excellent electronic and mechanical properties^{2–5} make them ideal candidates for a wide variety of applications such as transistors and logic operators, field emitters, scanning probe microscopy tips and in composites, (flexible) electronics, sensors, and solar cell technology.^{6–19}

A prerequisite for most of these applications is the ability to control the properties of the CNT structures. Often this means that aligned CNTs must be grown with specific properties tailored to the particular application. The ability to grow local CNT structures can be advantageous in some cases. For instance, local grown CNTs can act as transistors, field emitters, sensors, and interconnects. Local growth can be obtained by direct or indirect growth in which the latter requires an additional structuring step. Direct local growth of CNTs enables the growth on devices and substrates with temperature sensitive components while no intermediate structuring steps are needed. This greatly enhances the versatility of the process. Laser-assisted chemical vapor deposition (LACVD) is an attractive maskless process for local direct-growth of CNT structures.

The synthesis of CNTs is highly dependent on the process parameters such as temperature, process gases, catalyst, substrate, and time. The nature of the localized process makes it difficult to control some of the process parameters, most importantly temperature, in direct-growth processes.

Although many groups have published research regarding process control and optimization, temperature uniformity, *in situ* growth measurements, fast temperature response, etc., in LACVD for CNT growth, an overview of all the

different parameters influencing the synthesis and control of this method is still lacking. Many process parameters are available which makes it difficult to compare results. In this review paper, we aim to fill this gap by providing a comprehensive overview that combines the results of previous papers in a systematic manner. The main problems with process control and disadvantages of the technique are used as a starting point, where the solutions published are summarized and put into a logical order.

First a brief history is given with respect to general carbon nanotube growth methods that were developed initially. The focus of the paper being on controlled growth, the different chemical vapor deposition techniques are then discussed and their main (dis-)advantages mentioned. Combinations of several techniques, trying to use and combine advantages of the techniques are presented. Other methods for local growth of CNTs are presented and laser-assisted CVD in general is explained.

The remaining part of the paper is divided into two main parts. The first part summarizes the unique results regarding the structure, quality and type of CNTs specific for laser growth, with respect to the main elements of CNT growth by (laser-assisted) CVD: Catalyst and substrate, process gases, and thermal energy. The influence of the laser source is also discussed. The second part treats the research and solutions published with respect to enhancing the control over the process. An overview of attempts and successes to control specific properties, geometry, location and quality as well as techniques used to *in situ* monitor the growth are presented. Next, a brief overview of applications of CNTs specifically fabricated using laser-assisted CVD is given. We end with conclusions and our view of the future challenges of the research on LACVD: What is to be expected and what still needs to be done.

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A. Carbon nanotube growth methods: A brief overview

Before Iijima's pioneering work in 1991, it was already known since the late 1950s that carbon filaments or fibers could be catalytically grown using a chemical vapor deposition method (CVD).^{20–23} Already in 1976 Oberlin *et al.*²⁴ proposed a method for the catalytic decomposition of benzene on iron filaments producing tubular carbon nanostructures. However, Iijima's work, the first reported research declaring the growth of CNTs, did not use CVD but instead involved an arc-discharge method.¹ This process comprises a high current between two graphite electrodes. The CNTs were found in the soot of the graphite electrode and yielded both multiwall¹ (MWNTs) as well as single-wall CNTs (SWNTs) in a follow-up study.²⁵ The disadvantage of this method is that the CNTs are arbitrarily ordered and not aligned, making the method less suitable for many applications that require a certain structure and/or position on a substrate. Also, the temperatures involved in this process are very high and typically in the order of 3000–4000 °C.

Following up on this discovery, a group at Rice University used their laser evaporation method to successfully grow MWNTs in 1995.²⁶ The method, in which a pulsed laser was used to directly evaporate a graphitic target, was originally designed to produce metallofullerenes. Later in that year, the same group added metallic nanoparticles to produce single-wall CNTs.²⁷ The laser evaporation method is a relatively expensive method but has the advantage that high quality²⁸ SWNTs can easily be grown by controlling the reaction temperature.

B. Chemical vapor deposition for CNT growth

Producing carbon nanotubes by the CVD method is now adopted as the most widely used process. This method comprises a pressure controlled chamber where a hydrocarbon gas is catalytically decomposed on a metal catalyst at a temperature of about 500–1200 °C. Ultimately, the growth of CNTs by CVD requires three main elements, namely, energy, mostly in the form of an elevated temperature, a carbon feedstock gas, and a catalyst.^{29,30} The influence of all three components has been studied widely. The first reported CNTs grown by the CVD method was already in 1993.³¹ In 1996, Li *et al.*³² developed a method to grow aligned CNTs using iron nanoparticles as catalyst. The popularity of CVD over other methods is mainly because the technique uses relatively low synthesis temperatures, compared to the laser ablation and arc-discharge techniques. Because the diameter and, to some extent, the chirality of the nanotubes are dependent on the catalyst diameter or film thickness,^{33–37} the properties of the growth product are highly controllable. Also the ability to grown aligned CNTs is favorable since many applications such as field effect transistors and interconnect applications require alignment of the grown CNTs. Optimizing the advantages of the technique, a number of other CVD techniques for the growth of CNTs, such as plasma-enhanced CVD,^{38,39} aerosol-assisted CVD⁴⁰ and fluidized-bed CVD,^{41,42} were developed in the years thereafter.

Combinations of different growth techniques were developed as well. For instance, Kanzow *et al.*⁴³ developed a

method which combined the laser vaporization method with CVD to grow MWNTs. The laser was used for producing the catalytic nanoparticles, whereas the substrate was heated as in conventional CVD. Grobert *et al.*⁴⁴ used a similar method, where the laser was used only to deposit a thin metal catalyst film and aligned carbon nanotube bundles were grown from solid organic precursors. The group of Rummeli and Löffler developed both a method comprising a laser-assisted CVD with solid carbon as feedstock rather than a gas⁴⁵ as well as a laser ablation process combined with CVD.⁴⁶

Another possible advantage of a combined CVD process was discovered by Maehashi *et al.*⁴⁷ They developed a method to selectively remove particular CNTs through selective absorption of the exciting laser wavelength only by specific nanotubes after growing by thermal CVD. Similar methods were reported later, by using a free electron laser during growth to control the chirality of the grown CNTs (Ref. 48) and laser induced selective removal of metallic nanotubes.⁴⁹

Although CVD is the most widely used method to grow CNTs, the technique also has a number of limitations. First, the process requires a catalyst which generally remains in either the top or the root of the nanotube. This reduced purity can be a problem with respect to the properties of the CNT as well as specific applications. Second, the relatively low synthesis temperature decreases the structural quality of CNTs and results in a lower degree of graphitization. Nonetheless, CVD is still considered the most promising method to grow controlled nanotube structures for many applications, and it has also been suggested that SWNTs grown by the CVD method have less inferior properties than MWNTs.

Although not sufficient for optimal structural properties of the CNTs, the process temperatures are still relatively high, typically above 500 °C.⁵⁰ In both a hot-wall reactor as well as a cold-wall reactor, the complete substrate is, therefore, heated to these high temperatures, which makes it impossible to apply the technique to substrates and/or features that cannot withstand these temperatures. This can be problematic when the CNTs are to be implemented in a manufacturing line or product that has temperature sensitive features. A transfer step is then necessary, introducing more complexity and higher costs to the production line. Local CNT growth with localized heating would be a solution to this problem.

C. Methods for local growth of CNTs

Local growth of CNTs can be obtained by the localization of one of the three main components required for CNT synthesis: Catalyst, feedstock gas, and thermal energy.

The catalyst can be localized by depositing it locally⁵¹ or by creating a pattern through removing part of the catalyst layer. Usually this is done by an extra and expensive lithographic step.^{52–55} Localization of the carbon feedstock gas has been demonstrated,⁵⁶ but this is a process difficult to control.

The most promising method for localization of the CNT growth is to confine the required thermal energy to the area where the growth has to take place. A number of researchers have used microresistive heaters^{57–61} to induce the heat locally. Some groups succeeded in growing local CNT

structures on complementary metal oxide semiconductor-compatible metal electrodes⁵⁸ and heaters.^{60,61} Sosnowchik and Lin⁶² used microinduction to induce locally the thermal energy necessary for the CNT synthesis. A comprehensive overview of these and other techniques to localize heat for the growth of local nanotube structures is given in a review paper by Sosnowchik *et al.*⁶³

This review focuses on locally induced heat by a laser source. That means that CNT structures are grown with a chemical vapor deposition process but only at locations where the laser provides the necessary thermal energy to reach the CNT synthesis temperature. Using a laser as the heat source has the advantage that it is much more flexible than the approaches mentioned above, since the laser can be focused virtually anywhere on the substrate. In addition, this approach does not require the difficult fabrication and integration of microheaters near the growth side. The downside of this technique is the difficult process controllability. Table I lists several different properties, advantages and disadvantages, and process parameters of LACVD compared to conventional thermal CVD.

Considering the three main requirements for CNT growth: Catalyst and substrate, process gases, and thermal energy, the physics of laser-assisted CNT synthesis is different from conventional growth methods. For instance, catalyst reduction and structuring were found to be able to be created *in situ* without a pretreatment step in an inert environment. The synthesis gas can be influenced by the laser wavelength and the temperature created on the substrate by the Gaussian laser beam clearly has a very different profile than the flat and uniform temperature profile of a conventional hot-wall CVD apparatus. These and other parameters influencing growth are discussed in Sec. II. The control of the CNT synthesis using LACVD thus requires a different approach. The combination of noncontact local laser heating with fast temperature response and a nonuniform temperature distribution resulted in a variety of solutions to enhance controllability over the process. The enhanced versatility of the process

TABLE I. Comparison of different properties and process parameters between laser-assisted chemical vapor deposition and conventional chemical vapor deposition for carbon nanotube growth.

LACVD	CVD
Localized growth	Complete substrate growth
– Temperature sensitive components/substrates	– High quantity growth of CNTs
– Versatile process	– Necessity for pre patterning
– Writing patterns	
– Direction control	
Fast heating/temperature response	Low heating rate
– Catalyst structuring and activation <i>in situ</i>	– Catalyst pre patterning step
Nonuniform temperature distribution	Uniform temperature distribution (hot wall)
No direct control of temperature	Temperature set
Small amount of CNTs	Large amount of CNTs
– Fast response to changes in environment	– High inertial environment

over conventional growth methods, i.e., growing on small structures and writing lines and patterns or single tubes across a certain geometry, resulted in some creative and unique opportunities. This is discussed in Sec. III where we focus on process control. To understand the physics of the process, we will first briefly discuss the laser-assisted CVD process in general.

D. General laser-assisted CVD

Laser-assisted or laser-induced CVD for the decomposition of a certain precursor can be divided into two categories: Photochemical- or photothermal-LACVD.⁶⁴ Both processes are schematically depicted in Fig. 1. The first process, photochemical (or photolytic) LACVD is based on the decomposition of a precursor gas by selective excitation and breaking of the molecular bonds, typically with lasers in the visible or UV range, such as gas or excimer lasers. The result is that the decomposition takes place in the total laser-gas interaction volume. Generally, this process is used for thin film deposition at relatively low temperatures making the process ideal for the growth on temperature sensitive materials.⁶⁵ Photochemical LACVD has also been proposed for the production of microstructures⁶⁶ but the results did not yield well-defined deposits as a result of diffusion of the excited molecules.⁶⁷ Photolytic deposition of metal-carbonyls (such as $\text{Fe}(\text{CO})_5$) is a more widely used process for the deposition of thin metal films, with laser radiation wavelength typically below 350 nm. Other examples are the deposition of thin CrO_2 layers with UV lasers, requiring low deposition temperatures due to its metastable state and boron carbide films, using a CO_2 laser.⁶⁵

The second process, photothermal (or pyrolytic) LACVD is based on the thermal activation of the precursor by the laser beam. The process was developed in 1972 and among the first reports of this technique were the deposition of silicon by an infrared CO_2 laser⁶⁸ and the deposition of carbon using the visible radiation of an Argon ion laser.⁶⁹ Pyrolytic LACVD often requires high temperatures but enables the deposition of halogen compounds, hydrocarbons, and silanes.⁶⁴ This process solely uses the laser for heating the substrate on which the precursor material is then deposited. The material is only

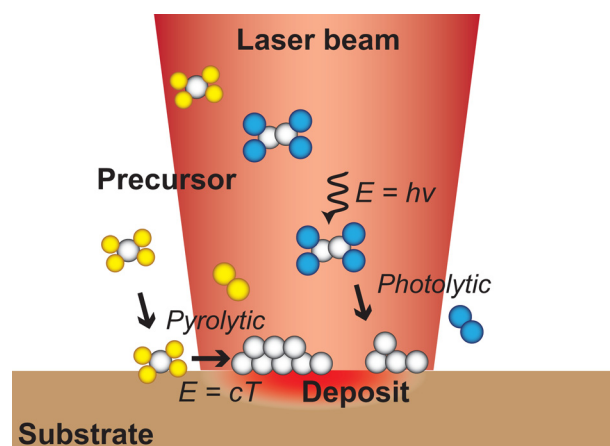


FIG. 1. Schematic for both laser-assisted chemical vapor deposition techniques: Pyrolytic and photolytic.

deposited where the temperature is high enough. Since laser beams generally provide a Gaussian distribution of irradiance on the focus spot, the feature size of the deposit can be smaller than the spot-size of the focused laser beam as long as the required temperature is only reached in a certain part of the center of the spot.⁷⁰ To obtain the smallest structural features, usually excimer lasers with Argon (193 nm) or Krypton (222 or 248 nm) are used due to their short wavelengths. Some LACVD processes consist of a combination of both previous processes where one of the two can dominate the deposition rate over the other. This combined process is called photophysical LACVD.

II. PARAMETERS INFLUENCING CARBON NANOTUBE GROWTH BY LOCALIZED LASER HEATING

When comparing laser-assisted synthesis of CNTs with a conventional CVD growth method, the main difference is the localized heat provided onto the substrate. However, with this core difference, other aspects of the process are influenced as well. Actually, all three main elements of the growth process are changed to a certain degree opening up new opportunities and remarkable results as well as imposing several problems. When comparing LACVD with other techniques, the resulting growth is assessed on structural and morphological quality of the carbon nanotubes. Raman spectroscopy is generally used to quantitatively assess the quality of the CNTs.^{71,72} At the same time, the type of nanotubes (single-walled or multiwalled), alignment, and growth direction can be viewed as a specific qualitative comparison between the different growth techniques.

The first reported research⁷³ on laser-assisted CNT growth showed the possibility of growing local CNT structures using a laser as the heat source. These reports also gave a first impression of the changed influence of process parameters on the resulting growth. Catalyst formation on the substrate, influence of gas and gas flows, and temperature distribution are among the parameters that are fundamentally changed. The laser source used in the process, its wavelength, irradiance, and whether it is a continuous-wave (CW) or pulsed laser, can have a noticeable effect on the resulting growth as well. In Fig. 2, a general schematic of laser-assisted growth for carbon nanotubes is given, demonstrating several variations. The laser source, providing the thermal energy necessary for CNT synthesis, can either be directed onto the substrate from the top side or the bottom side. The substrate is usually placed on a stage and can contain the catalyst, although catalyst precursors delivered through gas phase are possible as well. Several sensors, such as a pyrometer or *in situ* Raman can be used to monitor the process. The inset of the figure shows the two growth methods, common for CVD growth, base-growth, and tip-growth.

In what follows, we will describe the influence that the three main elements for nanotube growth—catalyst and substrate, gas, and thermal energy—has on the growth of carbon nanotubes by laser-assisted synthesis. Also the influence of the laser source is briefly discussed, as the wavelength, power, and type of laser can influence the growth kinetics as well.

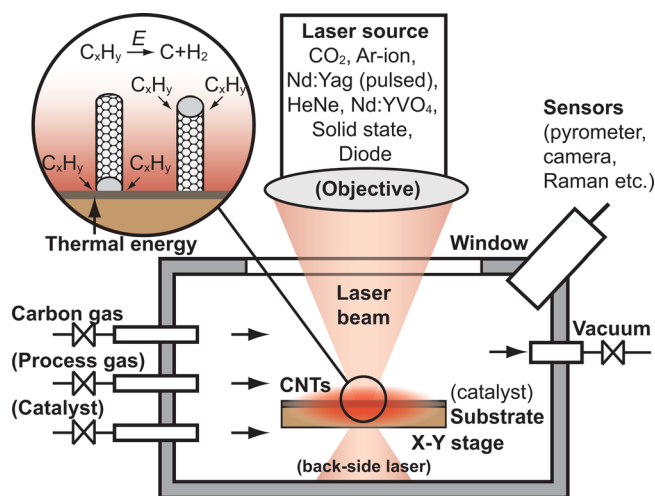


FIG. 2. General schematic for a laser-assisted chemical vapor deposition setup including the laser source, gas input, substrate and catalyst, stage, and sensors. Between brackets some variations or options are shown. The inset shows the two variations of CNT growth, base-growth (left) and tip-growth (right).

A. Catalyst and substrate

The laser heating allowed for a different method of catalyst deposition and preparation. In conventional CVD, it is common to have a catalyst preparation step, prior to the growth, which can take up to tens of minutes. In this step, the temperature is gradually ramped to the desired growth temperature in an inert gas, usually nitrogen. In laser-assisted CVD, this step can be much faster and even done *in situ*. Alexandrescu *et al.*⁷³ were the first to report on this. A CO₂ laser with a maximum power of 100 W was directed onto a silicon substrate. The catalyst precursor that was used was iron pentacarbonyl gas, Fe(CO)₅, which was formed *in situ* on the substrate as iron nanoparticles, by heating the substrate as well as the gas (photophysical heating). The authors reported straight, curved, and branched multiwall as well as single-wall CNTs and evidently showed the possibility of growing different types of CNTs using this method. By depositing and forming the catalyst directly from the gas state onto the substrate, they also proved the possibility of a fast *in situ* catalyst preparation step. Following their first report, the same authors then optimized the process by reducing the supply of catalyst and feedstock gas and investigated the separation of the catalyst deposition process from the CNT growth process.⁷⁴ Both the codeposition process as well as the two-step process resulted in high quality CNTs, but only with the codeposition process, a dense aligned MWNT film was obtained (see Fig. 3). Furthermore, the nanotube diameters that were obtained by the codeposition process were found to be considerably smaller than those obtained by the two-step process which was attributed to smaller catalyst nanoparticles in the case of codeposition.⁷⁴ This was explained by the fact that nanotube nucleation starts when the nanoparticles reach a critical diameter instead of the nanoparticles having their diameters determined by the duration of the preparation step.

Apart from the catalyst, the substrate and subcatalyst layer beneath the catalyst also influence the resulting growth. This is a result of the change in surface energy and wetting

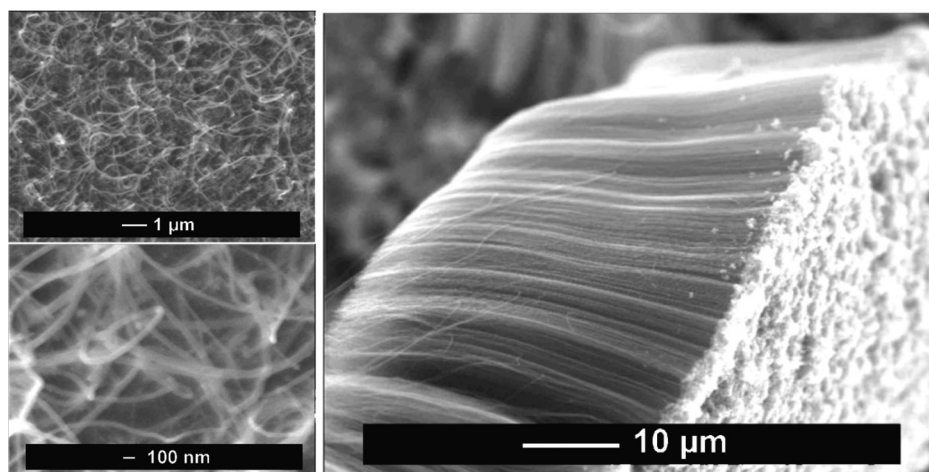


FIG. 3. Scanning electron microscopy (SEM) images of a carbon nanotube film synthesized in a two-step experiment (left) and SEM image of a densely packed aligned MWNT film. Reprinted with permission from F. Rohmund, R.-E. Morjan, G. Ledoux, F. Huisken, and R. Alexandrescu, *J. Vac. Sci. Technol. B* **20**, 802 (2002). Copyright 2002 American Vacuum Society (Ref. 74).

properties of the catalyst⁷⁵ as well as the different heat distribution through the subcatalyst layer and substrate.^{76,77} On top of that, transparency of the substrate for certain wavelengths is another property that significantly influences the growth method that can be used. The most commonly used substrate is silicon, although fused silica,^{76–78} graphite and grafoil,⁷⁹ and porous Al_2O_3 membranes^{80,81} were also used in combination with laser-assisted growth. Shi *et al.*⁸² synthesized suspended multiwall (650 °C) as well as single-wall (770 °C) nanotubes on inverse opal templates of silicon covered with a NiFe catalyst.

By using a substrate transparent for the laser wavelength, Chen *et al.*⁷⁶ were able to grow nanotubes from the backside of the substrate. However, the problem arose of how to efficiently heat up the very thin catalyst layer. As a solution, Chen *et al.* proposed using a light absorbing layer to support the catalyst. Their laser-assisted CVD process used a low power diode laser operating at 808 nm as the heat source. The glass substrate used was transparent to the laser wavelength and a layer of either carbon black, or commercial graphite inner coating was used to absorb the laser light. Chen *et al.* succeeded in growing arrays of well-aligned multiwall CNTs. Park *et al.*⁷⁷ used a quartz substrate in combination with a focused green (frequency-doubled) Nd:YVO₄ laser and used a combination of chromium and an aluminum buffer layer to absorb the laser light.

The subcatalyst layer codetermines the properties of the catalyst particles.⁷⁵ Oxides such as alumina (Al_2O_3) or silicon-oxide (SiO_2) are the most commonly used subcatalyst layers and they both prevent strong wetting of the metal catalyst ensuring the proper catalyst morphology while enhancing charge transport through catalyst and support.²⁹ The presence of the subcatalyst layer also narrows the size distribution of the catalyst.⁵⁰ The complex interactions that play a role in these mechanisms are not yet completely understood and as such also the role of local photophysical heating by laser irradiance is not clear. The influence of the laser-induced photons on the reactions, as well as the induced temperature gradient on temperature sensitive chemical reactions might not be neglected. At the same time, a

reduction of these stable oxides by thermal energy under hydrogen atmosphere is not expected.⁷⁵

B. Gas

Gas supply plays a significant role in the nanotube formation process. The binding energy of the carbon-containing gas typically determines the absorption rate of the gas on the catalyst and, therefore, indirectly influences the growth rate. Hydrogen, ammonia, and inert carrier gases influence the growth as well, by codetermining chemical and thermodynamic process parameters.⁵⁰ On top of that, the precursor gases can influence the catalyst reduction and restructuring,⁸³ effectively determining the CNT growth.

For some laser-assisted CVD growth, the photochemical heating of gases should also be considered. Ethylene has a resonant absorption at the CO₂ laser wavelength of 10.6 μm. This effect was used to coheat iron-pentacarbonyl gas, $\text{Fe}(\text{CO})_5$, and decompose this catalyst on the substrate⁷³ although follow-up research has shown that the mere thermal heating of the substrate provides sufficient energy for iron catalyst nanoparticles to form. In contrast, in thermal CVD, particularly at low temperatures, it is suggested that the preheating of the process gases can be useful to improve and enhance the growth process.^{84,85}

A few studies have been done linking the CNT quality to gas concentration for laser-assisted growth. Rohmund *et al.*⁷⁴ reported that high quality CNTs were only obtained when a significantly reduced acetylene concentration was used in the codeposition process, with respect to their two-step process. The result was a high quality dense MWNT film, and this was explained by a decreased growth rate. A lower carbon supply rate results in a lower growth rate and thus a lower defect formation at the same temperature.

Conversely, Bondi *et al.*⁷⁹ reported on more and denser tubes with increasing acetylene concentration. However, the growth took place in a statically filled chamber with no flow. The authors argued that a sufficiently large reaction-chamber ensured that the feedstock gas was not consumed during the experiment since the laser heating only resulted in a small

amount of CNT growth. However, the authors did not measure the quality of the nanotubes, only the amount and the density.

Morjan *et al.*^{74,86} investigated the influence of acetylene and ethylene precursor gas on LACVD growth. The authors reported that their experiments did not lead to any CNT growth by only using ethylene as a feedstock gas which was consistent with their previous work. As an explanation, the higher bonding energy of ethylene with respect to acetylene was given,⁸⁷ implying that the activation energy of the process is much higher, requiring higher temperatures to initiate growth. Consistent with thermal chemical vapor deposition,⁸⁸ an increase in ethylene concentration in laser-assisted CVD was found to increase the mean CNT diameter and the diameter size distribution to become broader,⁸⁷ see Fig. 4. At high temperatures, ethylene gas can decompose thermally resulting in more amorphous carbon deposition. This effect is larger when the ethylene gas is directly heated in the gas phase by the laser as well, which can explain the lower quality and larger diameter CNTs at higher ethylene concentration.^{86,87}

Some addition of ammonia-gas is commonly used to improve the growth by ensuring the presence of nucleation sites on the catalyst⁸⁶ and preventing the formation of amorphous carbon.⁵⁴ It can also be used to reduce the oxidized

catalyst and remove amorphous carbon. However, in combination with laser-assisted growth, too high concentrations of ammonia were found to decrease the quality of the CNTs.⁸⁶ This was likely a result of the low absorption of ammonia gas at the laser wavelength causing cooling effects.

Very high temperature gradients around the laser hot spot can also introduce local turbulences in the local gas supply. Particularly if the growth takes place in a chamber with steady-state pressure and gases, without a forced flow of process gases, turbulence or uncontrolled convection and local undersupply of carbon precursor might become a problem. However, to date, no systematic studies exist supporting this statement. Sufficient carbon feedstock supply to the hot spot is necessary to ensure stable growth, although Bondi *et al.*⁷⁹ argued that in the case of laser-assisted growth in a static chamber, the consumption of acetylene gas is so small that no noticeable depletion is occurring.

A specific example of exploiting the localized nature of laser-assisted growth combined with local gas control is given by the open-air apparatus of Kwok and Chiu.⁸⁹ Their approach was to separate the process gasses from the surrounding by generating different flows around the substrate. With this method, the authors were able to grow MWNTs on a quartz substrate in a controlled manner without the need for a vacuum chamber. A schematic and results are shown in Fig. 5.

As a final note, high flow rates directed onto the heated surface could also lead to temperature drops as a result of additional cooling effects. This effect is largest with high thermally conducting gases such as hydrogen and helium and was found to significantly affect process conditions in a thermal CVD setup.⁹⁰ Therefore, it is likely that this effect will be larger with smaller heated surfaces as is the case with laser-assisted growth. To overcome this problem, temperature control can be implemented which will be discussed in Sec. II.

C. Thermal energy

One of the main advantages of using a laser as the heat source is that very high heating rates are achieved and the catalyst activation process is much faster. The whole process is, therefore, much faster as a result. This is a direct result of the local concentrated photophysical heating of the substrate. Using a CO₂ laser in combination with ethylene gas, this can even be further enhanced by exploiting the laser absorption at the substrate–gas interface.⁸⁷

On the other hand, lasers have the disadvantage of introducing a nonuniform temperature distribution over the heated spot. This effect can be stronger for more tightly focused spots, due to the thermal conduction over the substrate. This is a direct result of the Gaussian distribution of the laser beam and often required solutions to the heat dissipation over and trough the substrate. The grown CNTs can, therefore, differ in type, quality, and amount throughout the laser-affected zone. This was first shown by Fujiware *et al.*⁹¹ The authors used an Ar-ion laser focused to a spot with a diameter of 5–40 μm as the heat source. Similar to the laser intensity profile, the resulting temperature profile had a Gaussian distribution as well. The corresponding growth

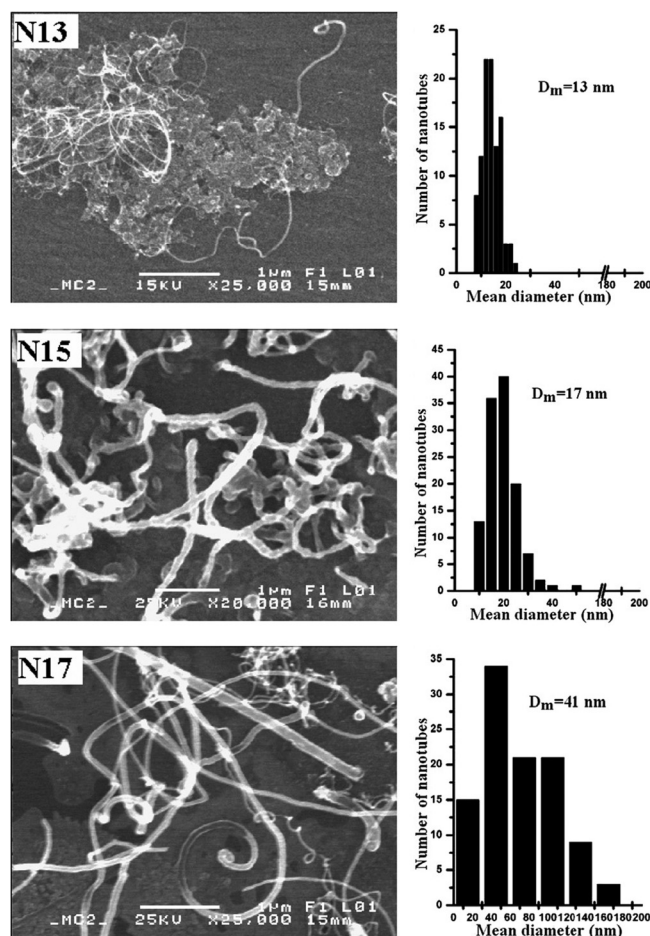


FIG. 4. SEM images of as-grown CNT films with increasing ethylene flow rates (up to bottom direction) and their respective diameter distributions (on the right side of each image). Reprinted with permission from I. Morjan *et al.*, *Infrared Phys. Technol.* **51**, 186–197 (2008). Copyright 2008 Elsevier (Ref. 87).

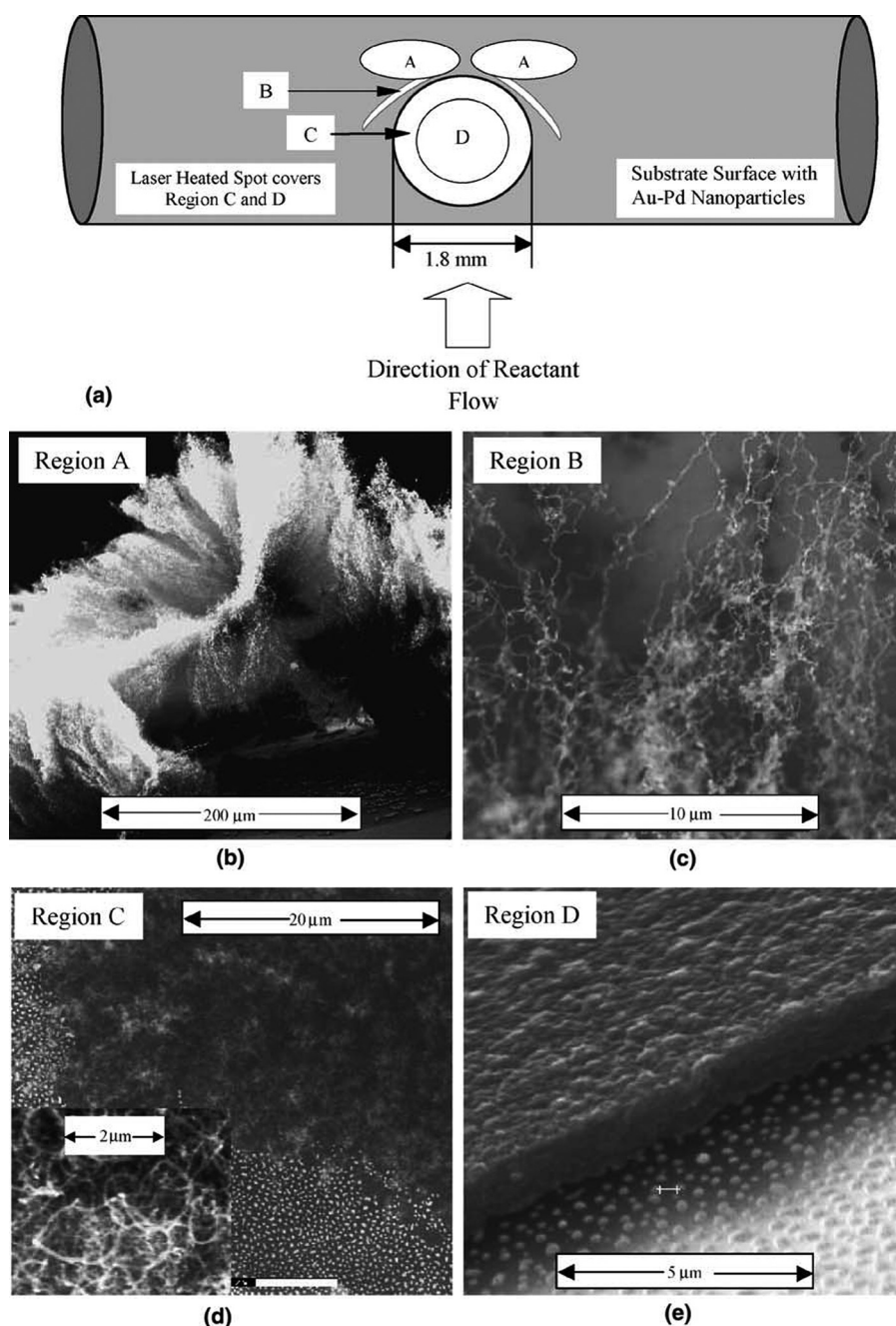


FIG. 5. (a) Schematic of the different carbon growth regions observed on the substrate after laser heating. SEM image of (b) dense packed carbon nanotube material, (c) scattered carbon nanotubes, (d) a region covering with a thin layer of ultradense carbon nanotubes, and (e) a thin layer of pyrolytic carbon covered the substrate and catalyst particles. Reprinted with permission from K. Kwok and W. K. S. Chiu, *Carbon* **43**, 437–446 (2005). Copyright 2005 Elsevier (Ref. 89).

resulted in the absence of CNTs in the center of the laser spot where the temperature was too high and SWNTs around the edges of the spot. By reducing the power of the laser beam, the authors succeeded in achieving growth over the complete focused laser spot. However, as expected, there was a difference in nanotube size, quality, and type over the radius of the spot.

Kasuya *et al.*⁹² suggested a method that tackled the problem of the heat dissipation through the highly thermally conductive silicon substrate that is often used. Because of the conductive silicon, a focused beam can result in a very flat temperature distribution much larger than the spot-size. To overcome these problems, the group proposed to use a

substrate with an “energy confining layer.” This layer consists of a 100 nm thick chromium layer to absorb the Nd:YAG laser source and a heat insulation layer of SiO₂ with a thickness of 1.5 μm, see Fig. 6. Using this layer, they successfully confined the heat into the area of laser irradiation which resulted in a rapid, 1 s, localized synthesis of SWNTs.

Similarly, in the research of Park *et al.*,⁷⁷ the chromium layer between the transparent quartz substrate and nickel catalyst acted as the light and heat absorbing layer while the aluminum buffer layer contributed to the uniformity of the growth, as shown in Fig. 7. By using iron as a catalyst, Park *et al.* also succeeded in growing MWNT pillars,⁹³ and by

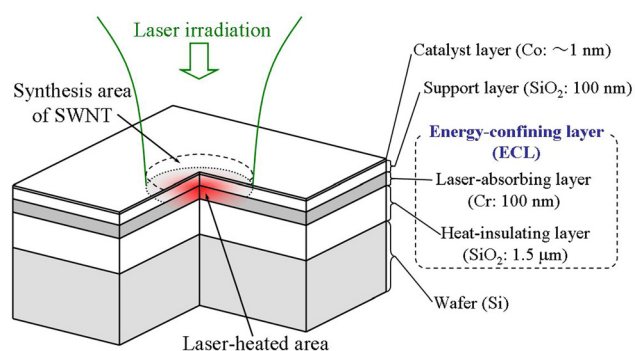


FIG. 6. Schematic of the laser-assisted CVD synthesis of SWNTs on a multilayer substrate with the energy confining layer as proposed in Ref. 92. Reprinted with permission from K. Kasuya *et al.*, Jpn. J. Appl. Phys., Part 2 46, L333–L335 (2007). Copyright 2007 The Japan Society of Applied Physics.

using a modified catalyst deposition process, high density SWNTs were grown as well.⁹⁴

Another solution to the problem of nonuniform temperature distribution could be to use beam-shaping or profiling. This technique has been successfully demonstrated in laser curing⁹⁵ and requires the inverse of the temperature distribution as an input in the beam profiler. A few examples are flat-top laser beams or donut shaped intensity profiles. To date, no research with laser-assisted growth of CNTs with these beam profiles has been presented.

D. Laser source

From a global point of view, thermal energy can be provided by any type of heat source. However, different energy sources can also influence the kinetics of the heating process. In fact, the laser type and wavelength could influence the resulting growth. Apart from the most commonly used CO₂ lasers, a wide variety of different laser sources have been reported to grow CNT structures, such as Ar-ion lasers,^{80,81,91,96} Nd:YAG lasers,^{78,92,97} diode lasers,^{76,98–100} and Nd:YVO₄ lasers.^{77,78,93,94} These reported laser sources all are CW lasers where the beam irradiates the substrate continuously for a certain duration.

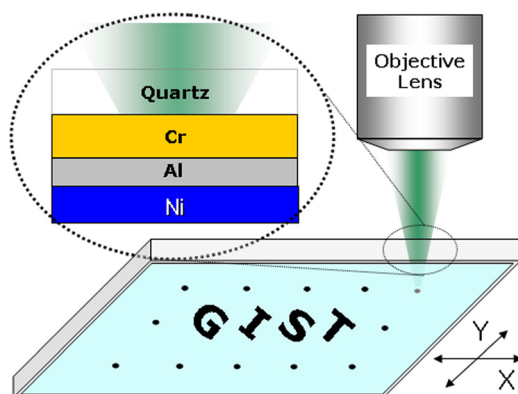


FIG. 7. Illustration of the direct laser writing of CNTs using the proposed LCVD method on multiple catalyst (Ni/Al/Cr) layers. Reprinted with permission from J. B. Park, M. S. Jeong, and S. H. Jeong, Appl. Surf. Sci. 225, 4526–4530 (2009). Copyright 2009 Elsevier (Ref. 77).

In 2008, Liu *et al.*¹⁰¹ reported for the first time CNT growth using a high-power pulsed-laser source instead of the conventional CW lasers. The reason for doing so was to be able to investigate kinetics of nucleation and growth of CNTs. Using a pulsed Nd:YAG laser, Liu *et al.* grew exclusively SWNTs with estimated growth rates between 10 and 100 $\mu\text{m/s}$ and a minimum nucleation time of 0.1 s. Similarly, Uchida and Yoshida¹⁰² used a pulsed Nd:YAG laser to grow SWNTs as well but combined this with resistive heating of the substrate.

A special case arises when a laser is used with a wavelength equal to the resonance frequency of the catalyst nanoparticles. This surface plasmon resonance effect of metal nanoparticles is the basis for the plasmon-assisted CVD process.¹⁰³ The laser-light is efficiently converted into heat inside the particles. In the research of Cao *et al.*¹⁰⁴ and Hung *et al.*,¹⁰⁵ a low-power 532 nm CW-laser is used to locally induce the surface plasmon reaction on nanoparticles. As a result, these particles are quickly heated to an elevated temperature, allowing the synthesis of CNTs on nickel¹⁰⁴ and gold particles.¹⁰⁵ Formally, the method described does not fit the laser-assisted CVD methods; nevertheless, it can be argued that it is in fact a CVD process using a low-power focused laser to stimulate the growth of CNTs. Actually, using this method, it has been demonstrated that local growth occurred only there, where the laser beam was focused and a metal nanoparticle was present, with even better confined heat distribution than in other laser-assisted CVD processes. As a result, the growth of CNTs on an SU-8 polymer substrate was demonstrated.¹⁰⁵

E. Part II: Summary

Laser-assisted heating significantly influences the process parameters in CNT growth. The rapid heating allows for a fast *in situ* preparation and deposition of the catalyst without the need for a pretreatment in an inert environment, while the substrate characteristics result in a number of interesting applications such as direct local growth initiated from the bottom.

Although focused laser spots tend to induce a widened and nonuniform temperature distribution, a number of solutions were proposed involving different, less thermally conductive, substrates, and energy confining layers. However, the resulting CNT growth might still vary over the radius of the heated area, and beam profiling could limit these effects.

The process gases and their partial pressure and ratio and flow rates significantly influence the growth, morphology, and structural quality of CNTs. Similarly to thermal CVD, this is a result of the binding energies that determine dissociation and absorption rates. For laser-assisted growth, however, ethylene and ammonia gas can be influenced by coheating of the gas phase as a result of the CO₂ wavelength absorbance of these gases, although it seems that the coheating has no or a negative influence on the growth. The general influence of gas on growth kinetics in combination with laser-assisted growth has not been investigated widely, and systematic studies are missing.

The type of laser that is used directly affects the resulting growth, as the coheating of ethylene with a CO₂ laser demonstrates. Numerous different lasers have been used where the power and wavelength generally are most important to the resulting growth. A pulsed-laser source opens up special possibilities including growth kinetics investigations.

III. PROCESS CONTROL IN LASER-ASSISTED CVD FOR CNT GROWTH

This section deals with the different control aspects of the LACVD growth. Using a laser as the localized heat source introduces difficulties with respect to process control but at the same time opens up different opportunities with respect to controlling, measuring, and monitoring the CNT growth process *in situ*. Because of the small area that is heated, the laser provides an almost instantaneous temperature response, making it much faster and more flexible in controlling the process than a global heating process. The laser source itself can also provide information on the process by for instance monitoring the reflection or a scattered Raman signal. However, the Gaussian distribution of the laser beam results in a nonuniform temperature distribution over the laser spot and surrounding, and control over the growth temperature is, therefore, not straightforward.

A. Temperature control

Temperature control is crucial to the control of the carbon nanotube growth. In conventional CVD systems, the temperature control is relatively straightforward. The process consist of either of a tube furnace heating both the furnace and substrate (hot wall reactors), or of a resistive or induction heater just below the substrate, heating only the substrate (cold wall reactors).¹⁰⁶ With laser-assisted CVD, the control of temperature is much less straightforward. Generally, not the complete substrate is heated so using a thermocouple or conducting another physical measurement of temperature within the laser affected zone is not possible. However, if the locally heated area is large and sufficiently uniform^{73,74,87} or if the thermocouple is close enough,⁹⁸ a first approximation of the growth temperature can be obtained.

1. Pyrometer controlled temperature

A better option is to use an optical pyrometer to measure the temperature within the laser spot directly^{74,80,82,87,89,97,101,107,108} if the laser-affected zone is large and uniform enough. Uniformity is necessary because the relatively small center of the laser spot should not have a temperature much higher than the overall spot temperature, since that would lead to biased temperature estimation. A number of different pyrometers are available, measuring in a range from 0–3000 °C and a spot diameter of 2 mm and larger. Liu *et al.* used a pyrometer in combination with a pulsed Nd:YAG laser source to investigate nanotube nucleation and growth.¹⁰¹ The 2 ms temporal and 2 mm spatial resolution of the two-color pyrometer enabled them to investigate the effect on sample temperature of a 50 ms

pulse. The calculated ramping rate was $\sim 3.3 \times 10^4$ °C/s, as the sample was heated to 900 °C in 25 ms. The pyrometer is generally used to be able to maintain a certain temperature in the laser spot at the surface but can also be used as feedback to dynamically change the temperature in time. This was demonstrated by Mahjouri-Samani *et al.*¹⁰⁸ by showing the ability to control and dynamically change the local temperature during growth.

2. *In situ* Raman-spectroscopy for temperature control

For a more precise control of temperature, an *in situ* Raman signal can also be used. This enables the direct measurement of the temperature of the substrate in the laser spot by measuring the Raman shift of the silicon substrate.¹⁰⁹ The spatial resolution is thus determined by the optics and ability to focus the Raman excitation laser while the temporal resolution is depending on the intensity of the Raman intensity. It has also been reported that Raman shift, peak width, and intensity of the radial breathing mode (RBM) are a function of temperature.¹¹⁰ Using these methods, Hung *et al.*¹⁰⁵ and Chiasi *et al.*⁹⁶ were able to determine *in situ* the temperature during CNT growth by laser irradiation. This is graphically shown in Fig. 8. Bock *et al.*⁷⁸ used the *in situ* Raman signal for a first approximation of the temperature. A downside of this technique is the difficult implementation of the Raman laser source in a growth setup. The high costs of the Raman laser source and setup are also contributing to the fact that not much research has been published with this technique yet.

3. Modeling of temperature

Next to the possibility of a direct measurement of temperature, using *in situ* Raman or applicable pyrometer, another approach to investigate temperatures involved in the

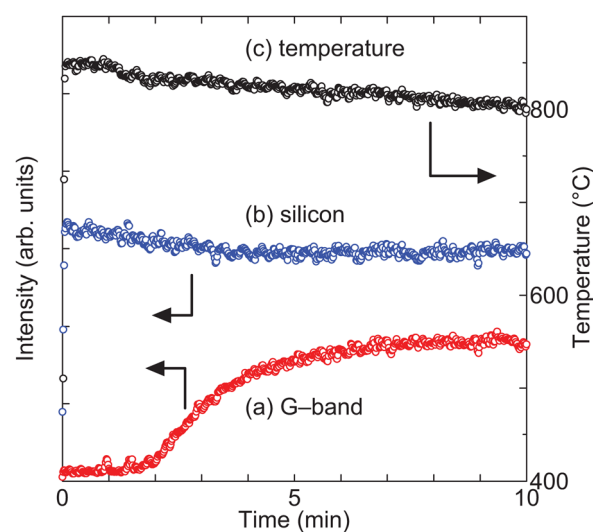


FIG. 8. Time variation of the silicon and the G-band peak intensities during the entire laser heating CVD process. While the silicon peak intensity (b) was almost constant, the intensity of the G-band (a) appeared after the supply of ethanol gas (at 1 min) and increased with time. Published under a CC BY-NC-SA license from S. Chiashi, M. Kohno, Y. Takata, and S. Maruyama, J. Phys.: Conf. Ser. **59**, 155–158 (2007). Copyright 2007 IOP Publishing Ltd. (Ref. 96).

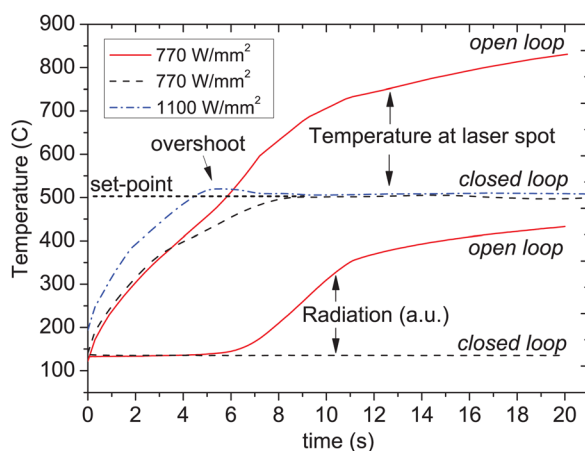


FIG. 9. Temperature at the laser spot as a function of time for the uncontrolled (black dashed) and radiation-controlled situation (red solid and blue dashed dotted). The set-point is shown with an overshoot. The radiation is also plotted for both situations. Reprinted with permission from Y. van de Burgt, Y. Bellouard, R. Mandampambil, M. Haluška, and A. Dietzel, *J. Appl. Phys.* **112**, 034904 (2012). Copyright 2012 AIP Publishing LLC (Ref. 100).

process is to use finite element method modeling (FEM) to calculate the corresponding temperatures. This was first demonstrated by Bondi *et al.*⁷⁹ who used a combination of computational fluid dynamics and finite difference modeling to implement the different heat transport mechanisms and convective fluid flow around the heated zone. The model also had the ability to include a scanning laser beam. A thermal camera was used to validate the model by comparing temperatures within the range of that camera. Kasuya *et al.*⁹² used a model without temperature dependent properties of the materials to investigate the temperature around the laser spot and as a function of time. In their case, the results should be interpreted qualitatively and mainly provide a first approximation of the rise time for the temperature and the spatial distribution of temperature around the laser heated spot. Neglecting convection and radiation effects, Cao *et al.*¹⁰⁴ used thermal modeling to describe their plasmon resonance process calculating the local temperature around a nanoparticle. The model included a frequency-dependent absorbed fraction of the laser power, which was highest at the surface plasmon resonance. Using an infrared photodetector, we developed a feedback control mechanism based on the thermal radiation as a first approximation of temperature, to control the temperature at the laser spot.¹⁰⁰ A finite

element method model was developed to investigate the temperature evolution in time for each experiment. The model included the time dependent laser irradiance and reflection signal calibrated with thermocouple information at the edge of the heated substrate. The model also contained temperature dependent Nusselt relations to include convection, as well as temperature dependent material properties of all the materials and gases involved. The modeled temperature at the laser spot as a function of time can be seen in Fig. 9, comparing the controlled case with the uncontrolled one.

B. Carbon nanotube diameter control

Since the beginning of CNT research, controlled synthesis has been widely investigated, and many attempts to optimize the growth have been made. Specifically chirality- and diameter-control is of great importance to be able to fully utilize the exceptional properties of CNTs in electronics and related fields.¹¹¹ The CVD process opened up more control of growth direction, alignment, location, and properties of the nanotubes, using a controllable metal catalyst as the basis for the growth. Ultimately, the research on CVD for CNT growth led to the well-known relation between catalyst particle size and diameter of the carbon nanotube.^{33–35} Even a direct relation between deposited catalyst precursor metal film thickness and nanotube diameter has been reported.^{36,37} Catalyst and morphology thus are an important control parameter in the controlled growth of nanotubes.

Numerous different catalysts have been studied but nickel, iron, cobalt, and their alloys, or compounds appear to be at the basis of most CNT growth. Laser-assisted CVD research shows a wide variety of catalysts as well. The early reports used $\text{Fe}(\text{CO})_5$ as catalyst precursor,^{73,74,79,86,87} but iron has been reported most.^{78,93,94,98–101,107} The control of catalyst morphology allows for a better control of the process, although there has not been a significant advantage of laser-assisted CVD over other CVD methods with respect to catalyst morphology control. In fact, the nonuniform temperature distribution most likely results in nonuniform size distribution of the formed nanoparticles and consequently a larger variety of CNT diameter and chirality. However, the quick temperature response to variations of the laser intensity allowed Mahjouri-Samani *et al.*¹⁰⁸ to modulate the SWNT diameter during growth. The resulting SWNT with changing diameter is shown in Fig. 10. The rapid temperature rise characteristic to

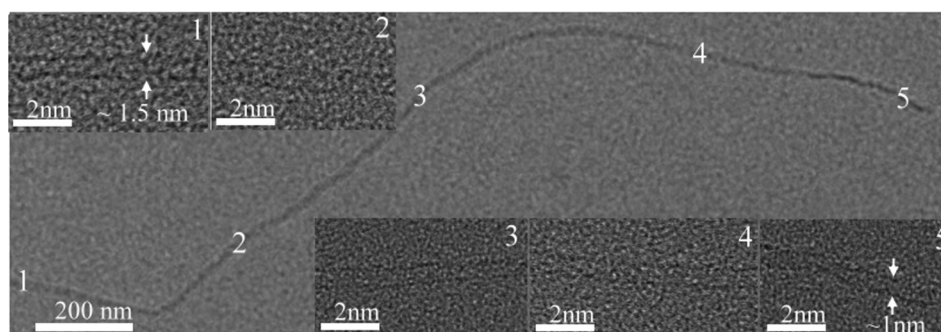


FIG. 10. TEM image of a $2\ \mu\text{m}$ long SWNT grown with a descending temperature profile. The close up views, (1–5), corresponding to the labeled areas of the tube, show about 0.5 nm variation in the diameter from one end to the other. Reprinted with permission from M. Mahjouri-Samani *et al.*, *Nanotechnology* **21**, 395601 (2010). Copyright 2010 IOP Publishing (Ref. 108).

laser heating could provide an advantage as research on the formation of nanoparticles using laser ablation techniques suggests.¹¹² Some groups have exploited laser-assisted growth combined with catalyst size control to better control the nanotube diameter distribution. For instance, Kwok and Chiu⁸⁹ used gold-palladium nanoparticles that were created in a separate process requiring a preparation step in nitrogen gas. This enabled them to have greater control over the diameter distribution of the nanoparticles. As expected, they showed a relation between the size of the nanoparticles and the nanotube diameter under constant laser radiation. Morjan *et al.* investigated CNT diameter with respect to process parameters as well. Well-defined iron-carbon composite nanoparticles with a narrow particle distribution were used as catalyst for the laser-assisted growth. The catalysts were produced by a pyrolysis of acetylene, ethylene, and iron-pentacarbonyl gas.¹¹³ Using precreated catalyst nanoparticles with a narrow diameter distribution allowed for a greater control over the resulting nanotube diameters.^{86,87} As an explanation for the observed widening of the nanotube diameter distribution, the tendency for the nanoparticles to cluster has been proposed. This tendency occurs when the substrate and catalyst have a higher temperature resulting in larger particles.⁸⁷ The temperature rises with higher laser energy but can also be influenced by other process parameters. Bondi *et al.*⁷⁹ also found a relation between nanotube diameter and process parameters, although

they used a gas phase catalyst, iron-pentacarbonyl. The authors found that a reduction of catalyst precursor gas pressure resulted in more growth and smaller diameters.

A more effective heating of substrate and catalyst has also been proven to positively affect the control over diameter distribution. Longtin *et al.*⁸⁰ succeeded in having a greater control over the diameter distribution by directly heating a laser-annealed nickel catalyst layer, electrochemically deposited within the pores of a porous Al₂O₃ membrane growing carbon nanofibers. In Table II, an overview of the catalysts used and corresponding research and results is given.

C. *In situ* process monitoring

To study kinetics and dynamics of the nanotube growth, *in situ* and real-time information from the growth process is essential. In thermal CVD nanotube growth, several techniques, such as using a displacement sensor,¹¹⁴ a shadow technique,¹¹⁵ or a probe beam reflection technique,¹¹⁶ have been used for that purpose. The shadow technique links the dynamically changing intensity of a light source on a CCD chip with the length of the vertically aligned nanotube forest. Dynamic reflection techniques use a laser beam which is focused on the growth side and reflection is measured to study the growth rate, size, and other dynamic properties.^{116,117} To obtain similar *in situ* information about the

TABLE II. Overview of research published on laser-assisted CVD for carbon nanotubes.

Laser (focus)	Power	Substrate	Catalyst	Carbonaceous gas (process gas)	Temperature range	Time range	Results	References
CO ₂ unfocused	100 W	Silicon	Fe(CO) ₅	C ₂ H ₂ , C ₂ H ₄	770–860 °C	3 min (15–20 min)	MWNT (aligned)/SWNT	73 and 74
Ar-ion focused	180 mW	Silicon	Fe(NO ₃) ₃ ·9H ₂ O + MoO ₃ + Al ₂ O ₃	C ₂ H ₅ OH		1 min	SWNT	91
CO ₂ unfocused	30 W	Quartz	Au-Pd	C ₃ H ₈	1000–1400 °C	10 min	MWNT	89
CO ₂ focused	100 W	Silicon, graphite/graphite	Fe(CO) ₅	C ₂ H ₂ (Ar)	1130 °C	200 s	MWNT	79
CO ₂ /Nd:YAG (un)focused	20–25 W 60 W	Silicon	Fe-Mo-Al ₂ O ₃	C ₂ H ₂ (NH ₃)	690–720 °C	3–6 min	SWNT	97
CO ₂ unfocused	20–45 W	Silicon	Ni-Fe	C ₂ H ₂ (NH ₃)	650–770 °C	5 min	SWNT MWNT	82
Nd:YAG focused	50 mW	Silicon	Co	C ₂ H ₅ OH	~800 °C	1 s–10 min	SWNT	92
CO ₂ unfocused	80 W	Silicon	Fe(CO) ₅ , FeC	C ₂ H ₂ , C ₂ H ₄ (NH ₃)	800–900 °C	5 min	MWNT	86 and 87
Diode focused	2 W	Glass, ITO	Fe-Mg	C ₂ H ₂ (Ar)	<600 °C	5–30 s	MWNT	76
Ar-ion unfocused	~1.5 W	Al ₂ O ₃	Ni	C ₂ H ₄	790–1848 °C	750 ms–5 s (360 s)	Nanofibers aligned	80 and 81
Solid state focused	20 mW	Fused silica	Ni	CH ₄ , C ₂ H ₄		45 s	MWNT	104
HeNe/Ar-ion focused	30 mW 40 mW	Silicon	Fe-Co, Mo-Co	C ₂ H ₅ OH	800–830 °C	15 min	SWNT	96
Nd:YAG (pulsed) unfocused	600 W	Silicon, SiO ₂	Fe, ferritin	CH ₄ , C ₂ H ₄	650–770 °C	50 ms–30 s	SWNT/bridge	101
Nd:YVO ₄ focused	57–125 mW	Quartz Al-Cr	Ni	C ₂ H ₂ (H ₂)/C ₂ H ₄ (H ₂)		60 s (1–180 s)	MWNT aligned/SWNT	77, 93, and 94
Diode focused	5–30 W	Silicon, Al ₂ O ₃	Fe	C ₂ H ₄ (Ar, H ₂)		9–180 s	MWNT aligned/SWNT	98–100
Solid state focused	5 W	Si/glass	Au	CO (Ar, H ₂)	1180 °C	10 min	SWNT	105
CO ₂ unfocused		Silicon, SiO ₂ /Ru	Fe	C ₂ H ₂ (NH ₃)	550 °C		SWNT bridge	107
CO ₂ unfocused		Silicon, SiO ₂	Al-Fe-Al	C ₂ H ₂ (NH ₃)	450–650 °C	1–4 min	SWNT (aligned)	108
CO ₂ focused	5 W	Silicon	Fe	C ₂ H ₄ (Ar, H ₂)	~660 °C		MWNT	123
Nd:YAG (pulsed)		Silicon	Co-Fe	C ₂ H ₅ OH			SWNT	102
Solid state focused	10–180 mW	Fused silica, Al ₂ O ₃	Fe	C ₂ H ₂	~700–900 °C	2 min	MWNT	78

CNT growth process using LACVD, the same laser beam used for the local heating can be used, as we have recently showed by measuring growth kinetics in LACVD.¹²⁷

The laser beam used for heating the substrate can also be used for a number of other measurement techniques. Using *in situ* Raman, for instance, Chiashi *et al.*⁹⁶ were able to characterize SWNT growth as a function of time as shown in Fig. 8. The authors were successful in growing SWNTs using a HeNe laser but for the *in situ* Raman experiments, the Raman-excitation Ar-ion laser was also used as the heating source. Hung *et al.*¹⁰⁵ used a similar *in situ* Raman process to investigate and monitor the growth of the SWNT and coinduced metal oxide process as well as the temperatures involved during growth. By measuring the reflection of the laser beam, Haluška *et al.*⁹⁹ identified different stages of CNT growth and related those to the *in situ* measurement of different sensors. The information from the reflection of the laser beam provided a first approximation of the growth product. A drop in reflection signal corresponded to the growth of nanotubes but a further drop in this signal was identified as amorphous carbon deposition as a result of the increased laser absorption of the CNTs which resulted in overheating. This is schematically shown in Fig. 11. In a follow-up research, we developed a unique method to identify the onset of catalyst formation and activation by monitoring the fluctuation of the reflected laser beam.¹⁰⁰ Bock *et al.*⁷⁸ reported on optical feedback mechanisms during growth of MWNTs. *In situ* Raman and reflection spectroscopy are related to the growth products. A strong positive feedback was observed during different stages of the growth. More laser energy is absorbed as a result of CNT growth, corresponding to previously found results by Haluška *et al.*,⁹⁹ so the temperature increased and this eventually resulted in amorphous carbon deposition above 900 °C.

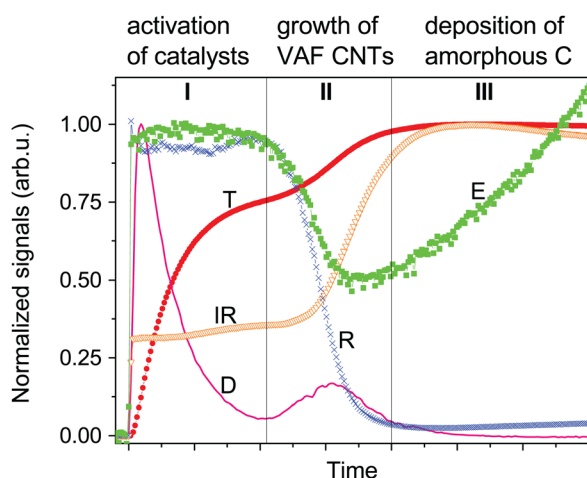


FIG. 11. Normalized *in situ* signals that characterize the growth process. The red bullets, the blue crosses, the orange triangles, and the green squares represent the temperature (T), the intensity of reflected light (R), the IR detector signal (IR), and the visible light detector signal (E), respectively. The pink curve displays the time derivative of the temperature signal (D). The Roman numbers represent the process regimes. Reprinted with permission from M. Haluška, Y. Bellouard, Y. van de Burgt, and A. Dietzel, *Nanotechnology* **21**, 075602 (2010). Copyright 2010 IOP Publishing (Ref. 99).

D. Localization and direction of carbon nanotube growth

One of the major reasons for the popularity of CVD over other CNT growth techniques is the high controllability over properties, alignment, and growth direction of the resulting CNTs. Yet, control over specific position and direction sometimes proves to be challenging, especially when integrating the process with other processes and (temperature-) sensitive materials. The unique nature of laser-assisted CVD growth has been found to show some interesting solutions to enhance the controllability of the specific position and direction of the grown CNT structures.

1. Local aligned growth

Numerous applications require specific alignment of the CNT structures. Particularly, vertically aligned CNT structures are preferred. Rohmund *et al.* were the first to demonstrate aligned CNTs using LACVD.⁷⁴ They showed films of vertically aligned multiwalled carbon nanotubes of extremely high packing density. Later, Haluška *et al.* grew

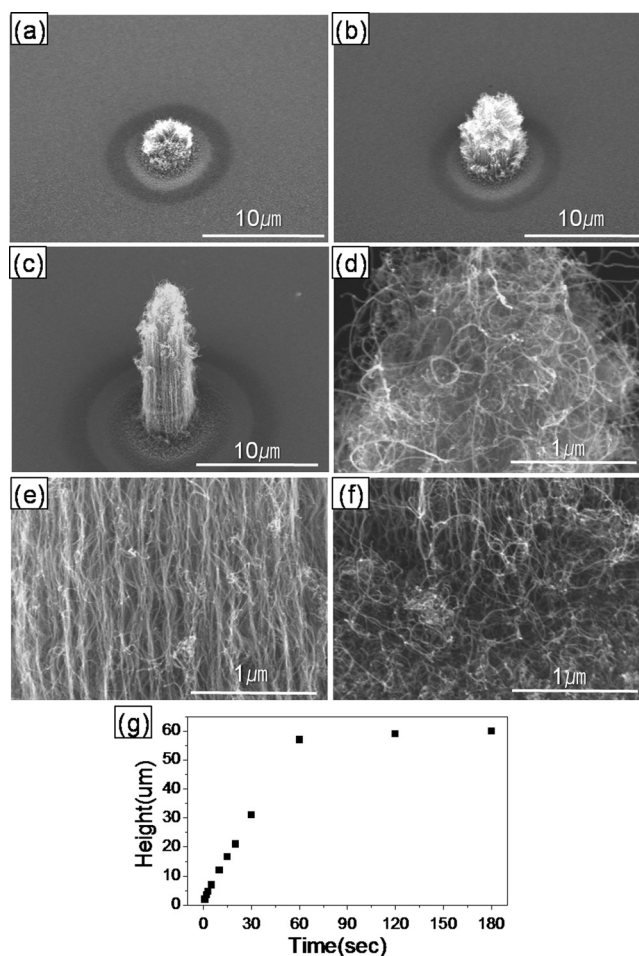


FIG. 12. SEM images of position-controlled CNTs produced using LACVD with growth times of (a) 1 s, (b) 3 s, and (c) 15 s. The magnified images show the (d) top, (e) middle, and (f) bottom of the VA-CNT pillar in (c). (g) Variation of the height of VA-CNT pillars with respect to irradiation time. Reproduced with permission from J. B. Park *et al.*, *Nanotechnology* **20**, 185604 (2009). Copyright 2009 IOP Publishing (Ref. 93).

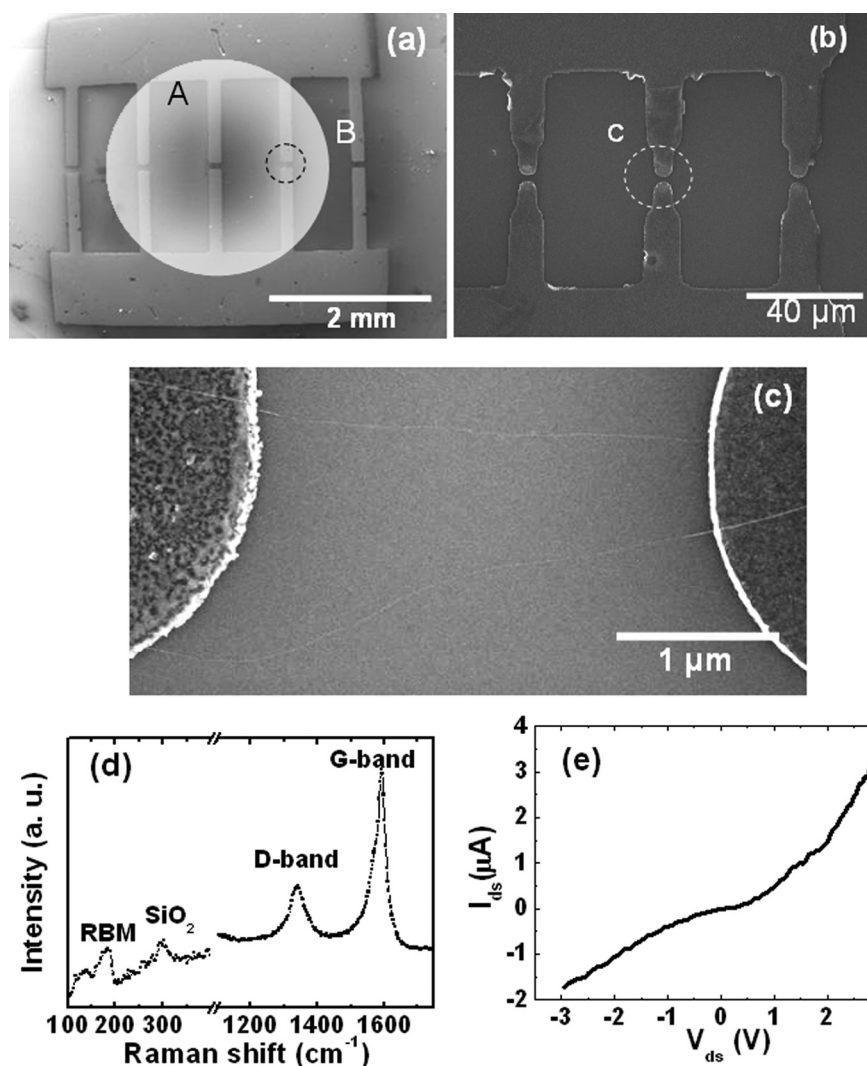


FIG. 13. (a) SEM micrograph of patterned Mo electrodes. Circle “A” is the typical unfocused 2 mm CO₂ laser beam irradiated on the substrate, while circle “B” is the typical focused laser beam with beam size of 340 μm using a 10 cm ZnSe lens. (b) Magnified electrode pairs inside circle “B” shown in (a). (c) SEM micrograph of two SWNTs bridging the electrodes inside circle “C” shown in (b). (d) Raman spectroscopy of SWNTs shown in (c). (e) I - V curve of the SWNTs shown in (c). Reprinted with permission from J. Shi *et al.*, Appl. Phys. Lett. **89**, 083105 (2006). Copyright 2006 AIP Publishing LLC (Ref. 97).

vertically aligned single-walled and multiwalled carbon nanotube forests⁹⁸ and Bock *et al.* reported on radially aligned multiwalled CNT structures.⁷⁸ Also large mats of aligned carbon nanofibers were reported.^{80,81}

However, laser-assisted CVD opened up the possibility to grow local aligned CNT structures, with a structural size in the order of the laser spot-size. Chen *et al.* were the first to show local aligned CNT structures.⁷⁶ The authors reported on well-aligned multiwalled carbon nanotube arrays on glass, using a back side laser illumination in combination with a carbon black layer. Park *et al.*⁹³ also used back side laser illumination to grow vertically aligned pillars of MWNTs. The pillars were roughly 4 μm in diameter and grew with 1 μm/s to a height of around 60 μm, see Fig. 12.

Apart from local vertically aligned growth, it can also be useful to align the CNTs in any other arbitrary direction. It has been known for some time that an electric field can align the CNT growth along the field lines.^{118,119} However, applying an electric field over the growth area is not easy. Other groups have shown that also a flow of process gasses could

be used to align the nanotube growth in the direction of the flow.^{87,120,121}

To combine the localized laser-assisted growth process with direction control would even further enhance the possibilities for future nanotube-based electronic devices. The control of alignment and direction of CNT growth using LACVD was first demonstrated by Bondi *et al.*⁷⁹ They used an electric field in combination with H₂ gas flow to align the tubes in a certain direction.

The group of Yongfeng Lu investigated the ability to grow suspended aligned CNTs over a variety of structures and geometries. By exploiting the ability of the laser to heat suspended structures, smaller than the laser spot-size, they were able to grow (single) CNTs bridging electrodes or other suspended geometries.^{82,97,107,108} They reported on SWNTs bridging two Mo electrodes using an unfocused as well as a focused CO₂ laser in combination with an electrical field.⁹⁷ The field applied was varied between 1 and 1.5 V/μm⁻¹. An ampere meter was used to monitor the completion of the bridging, when a current flow was observed. This typically

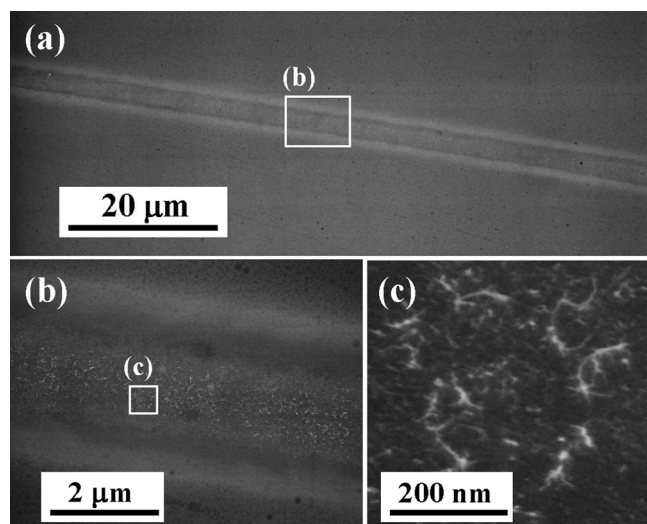


FIG. 14. SEM images of line-patterned synthesis of SWNTs by scanning of laser-irradiation spot: (a) Entire region, (b) enhanced area, and (c) highly magnified image of enhanced area. Reprinted with permission from K. Kasuya *et al.*, Jpn. J. Appl. Phys., Part 2 **46**, L333–L335 (2007). Copyright 2007 The Japan Society of Applied Physics (Ref. 92).

took around 20–30 s. The result is shown in Fig. 13. Following up on this, the group also reported on the local growth of semi-conducting SWNTs bridging two Ruthenium electrodes, using optical near-field effects in the laser-assisted CVD process.¹⁰⁷ A DC voltage of $1 \text{ V}/\mu\text{m}^{-1}$ assisted the self-aligned growth. The growth took place at 550°C , considerably lower than commonly reported for LACVD. A recent article¹²² provides a comprehensive summary of the findings and (laser-assisted) techniques developed in their laboratory.

Using a focused CO_2 laser, Ruan *et al.*¹²³ grew forests of CNTs directly on small suspended structures. They succeeded in growing tens of nanometers thick MWNTs on suspended silicon microstructures smaller than the laser spot-size using iron as catalyst. Due to the low thermal mass and heat dissipation of these small structures, the authors only required a low power CO_2 laser source.

The plasmon resonance process described by Hung *et al.*¹⁰⁵ was used to create a method to control the growth and direction of suspended carbon nanotubes moving the laser in three dimensions. It is believed that the large temperature gradient generated in the vicinity of the laser spot was responsible for the direction controlled growth.

2. Writing lines and patterns

Another advantage of using a laser as the localized heat source over other local heat sources such as microresistive heaters is the flexibility to heat any part of the substrate desired and to move the substrate with respect to the laser spot while growing. Bondi *et al.*⁷⁹ were the first to use this

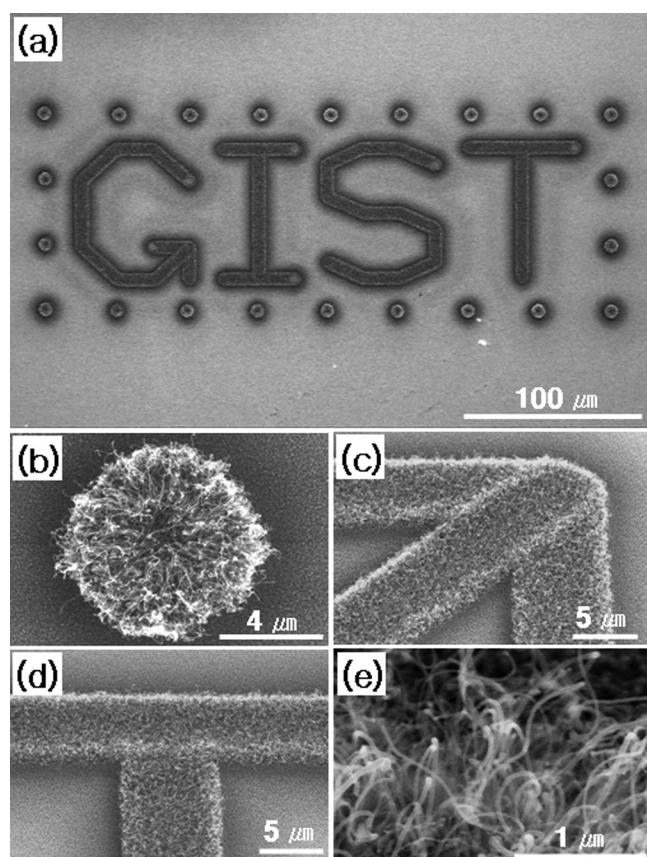


FIG. 15. Scanning electron microscope images of the CNTs: (a) dot and line patterns, (b) magnified view of a dot pattern, (c) and (d) magnified views of cross lines, and (e) view of individual CNTs in typical CNT patterns. Reprinted with permission from J. B. Park, M. S. Jeong, and S. H. Jeong, "Direct writing of carbon nanotube patterns by laser-induced chemical vapor deposition on a transparent substrate," Appl. Surf. Sci. **225**, 4526–4530 (2009). Copyright 2009 Elsevier (Ref. 77).

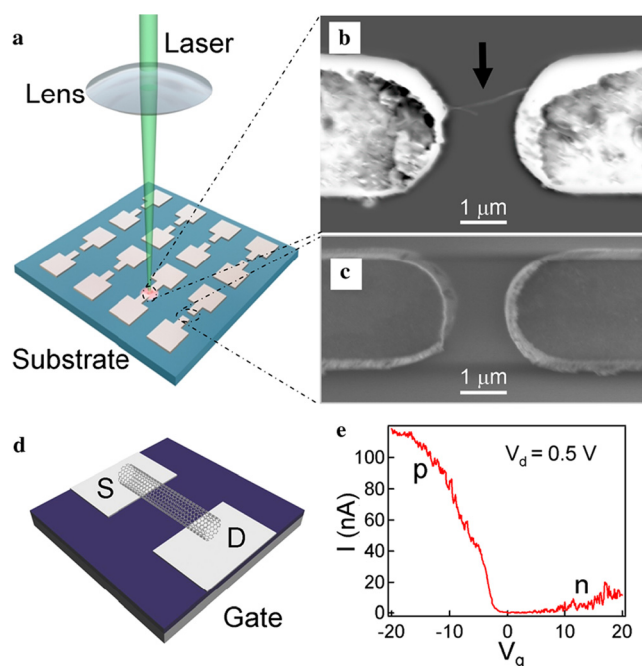


FIG. 16. (a) Schematic of local direct-writing of SWNTs for device applications. (b) An *in situ* contacted nanotube bridging two electrodes. Arrow identifies the nanotube. (c) No nanotube growth from adjacent electrodes outside the heating zone. (d) Schematic diagram of a back-gated SWNT field-effect transistor. (e) I - V_g curve of the transistor exhibiting ambipolar behavior. Reprinted with permission from Z. Liu *et al.*, Appl. Phys. A: Mater. Sci. Process. **93**, 987–993 (2008). Copyright 2008 Springer Science+Business Media (Ref. 101).

advantage and were able to write dot and line patterns of CNTs with a width of $200\text{ }\mu\text{m}$ using a focused CO_2 laser. Their approach was to scan multiple times with a high speed rather than one scan at low speed. It appeared this method resulted in less unwanted and uncontrolled growth at the laser spot. However, the influence of the laser beam on already grown CNTs was not yet investigated.

Combined with their energy confining layer, Kasuya *et al.*⁹² were able to write thin $2\text{ }\mu\text{m}$ wide SWNT lines with a write speed of $1\text{ }\mu\text{m/s}$ using their focused Nd:YAG laser. In Fig. 14, SEM pictures of the resulting growth are presented. Park *et al.*⁷⁷ succeeded in writing dense multiwalled dot and line CNT patterns below $10\text{ }\mu\text{m}$ in size. Their results are depicted in Fig. 15. The energy absorbing layer that was used proved to be critical in their results as well. It ensured the uniformity of growth, reducing the sensitivity of the catalyst layer to local temperature variations.

E. Part III: Summary

Process control in laser-assisted CVD growth of CNTs is essential. As CNT synthesis depends largely on process conditions and particularly temperature, a well-controlled temperature is crucial. A thermocouple, optical pyrometer, or Raman signal can be used to measure temperature directly where the Raman is most precise but also most difficult to implement and most expensive. With no direct temperature measurement, thermal modeling can be used to calculate temperatures involved in the process afterward or to predict the temperature upfront. Using the fast temperature response in combination with direct temperature measurement, the growth temperature can be instantly varied. This enables direct control over the diameter of the CNT. Other attempts to increase control over the diameter of the CNTs generally consisted of more control over the catalyst size and morphology.

A direct result of the laser-assisted CVD process is the ability to *in situ* monitor the process. The dynamically changing reflected laser signal can be used to investigate growth kinetics or even be used as a Raman signal, characterizing CNT quality growth as a function of time.

Finally, the localized nature of the laser-assisted growth enables local aligned growth as well writing lines and patterns on substrates with temperature sensitive components making it a highly versatile process.

IV. APPLICATIONS

Localized controlled CVD for CNT growth has the advantage that it is a highly flexible process easily integrated in the production process; however, actual functioning applications with CNTs are still relatively sparse. Most likely, this is the result of the practical integration of conventional CNT growth processes and the insufficient controllability in the case of LACVD growth. The ability to write patterns and grow CNT structures locally wherever desired does enhance possible future applications. Laser-assisted CVD growth has a significant advantage over conventional CVD heating with respect to the localized heat. This opens up opportunities for applications to directly grow the CNT structures on substrates containing heat sensitive parts rather than separating

the process into a growth and transfer step. This flexibility was demonstrated, for instance, by Liu *et al.*¹⁰¹ see Fig. 16. They developed a nanotube field effect transistor that showed ambipolar behavior using their pulsed laser direct-write method. The figure clearly shows the ability to direct the laser on a certain position of the structure, restricting the growth to that location. Chen *et al.* tested the field emission properties of their array of well-aligned multiwall CNTs on a fluorescent screen.⁷⁶ The result is shown in Fig. 17. The flexibility of the laser assisted CVD process enables them to write any pattern or text with fluorescent CNT structures, without having to perform a lithography or transfer step. Using the fast temperature response of localized laser

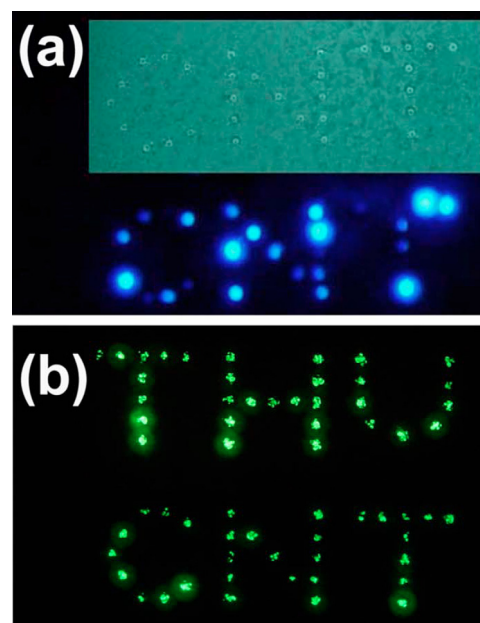


FIG. 17. Field emission patterns on fluorescent screen. (a) Upper, optical image of the laser direct writing carbon nanotube cathode on the carbon black layer; lower, optical image of field emission patterns on fluorescent screen (applied voltage: 1700 V; digital camera: $F = 4.0$, $1/40\text{ s}$). (b) Optical images of field emission patterns on fluorescent screen from the carbon nanotube cathode on the commercial graphite inner coating layer (applied voltage: 1400 V; digital camera: $F = 4.0$, $1/200\text{ s}$). Reprinted with permission from Z. Chen *et al.*, Appl. Phys. Lett. **90**, 133108 (2007). Copyright 2007 AIP Publishing LLC (Ref. 76).

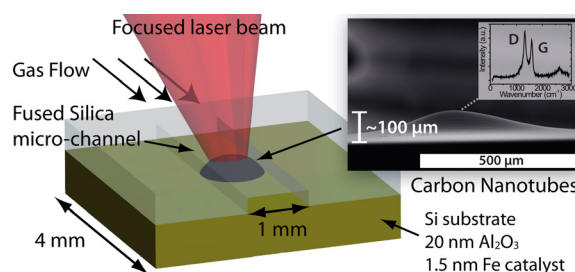


FIG. 18. Schematic of the direct local growth of carbon nanotubes inside a sealed microchannel. The inset shows a SEM picture of a hill of aligned CNTs created with the direct local growth method inside the microchannel. Also visible is the Raman spectroscopy signal measured at the center of the hill, indicating the presence of mainly multiwall CNTs. Reprinted with permission from Y. van de Burgt, A. Champion, and Y. Bellouard, AIP Adv. **3**, 092119 (2013). Copyright 2013 AIP Publishing LLC (Ref. 124).

heating, Mahjour-Samani *et al.*¹⁰⁸ fabricated a single carbon nanotube diode that was integrated in electrodes to form a field-effect-transistor. Decreasing temperature during growth resulted in an increase of nanotube diameter, which accounted for the diodelike behavior. As a final example, we recently demonstrated the direct growth of aligned carbon nanotube structures inside a microchannel.¹²⁴ The ability of the laser to heat the growth site through a transparent cover could prove useful in fabricating *in situ* CNT structures that could act as sensors or filters for microfluidic and lab-on-chip devices. This is schematically shown in Fig. 18.

V. CONCLUSIONS AND PERSPECTIVES

Laser-assisted CVD growth of carbon nanotubes has developed into a very attractive process for local, rapid, and well defined growth of CNT structures. The ability to grow virtually anywhere on a substrate, write patterns and lines, inside microchannels and close to temperature sensitive elements and components opens up new application areas for CNTs. Although it is not a new technique, a number of opportunities but also new problems specific to the growth of CNTs with laser-assisted CVD arose. The influence of the laser on the growth characteristics was found to be significant. Catalyst preparation and substrate selection introduced unique opportunities specific for laser-assisted growth. Also, gas phase heating by a specific laser wavelength and the influence of different types of lasers was investigated. Most dominantly though, process control was proven to be challenging. Process control is essential for control over the growth product and properties and as such ultimately over possible applications. Several solutions were developed regarding temperature-, alignment- and position control. These attempts greatly enhanced the ability to tune the properties of the CNTs, as the demonstration of diameter control by fast temperature control has proven. Benefiting from the laser signal, primarily used for the heating, several direct measurements of the growth could be extracted. *In situ* Raman spectroscopy, for instance, provides a direct measurement of the structural quality of the CNTs. On top of that, the reflected signal can be used for first order measurements of growth characteristics such as length and growth rate.

The next step in laser-assisted growth would, therefore, be to use the technique itself to further understand and unravel the mechanism of CNT growth by laser-assisted CVD. As the nature of the localized laser-induced growth is different than for other CVD techniques, it is crucial to understand the growth mechanisms, dynamics, and other kinetics to fully utilize and optimize the capabilities of this technique. As recent successes on carbon nanotube computing have proven,¹⁹ the ability to grow controlled local suspended CNTs on specific positions might be a next step. Laser-assisted CVD has a major advantage in selectively heating the growth site and the ability to grow single suspended CNTs, capable of displaying transistor behavior. In that perspective, we would expect LACVD to be a basis for cheap printed full carbon electronics, especially for flexible electronics and/or prototyping, allowing the user to quickly produce specifically designed devices, competing with

classical techniques by easiness and cheapness, not by fabrication volume.

A further enhancement of the local gas flow growth of Kwok and Chiu⁸⁹ could be the development of a miniaturized reaction chamber with incorporated laser to be able to selectively grow CNTs on a large wafer or device. This way, local, aligned structures of carbon nanotubes can be created without the need for a static CVD chamber, anywhere desired. Of course, scientific focus has been shifting toward other molecular carbon structures such as graphene where we would expect the laser-assisted CVD method could also provide major advantages for local, controlled growth as some first results already suggests.^{125,126}

A lot of progress has been made to enhance CNT growth control, though controlled growth of individual CNTs with predetermined specific morphological, chemical, and electrical properties remains a challenge. Nevertheless, current developments on understanding the rate-limiting mechanisms, including our own work, greatly enhance the knowledge of underlying mechanisms of CNT growth, thus enabling further enhancements on specific control.

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- ¹S. Iijima, "Helical microtubules of graphitic carbon," *Nature* **354**, 56–58 (1991).
- ²M. R. Falvo, M. R. Falvo, G. J. Clary, R. M. Taylor, V. Chi, F. P. Brooks, S. Washburn and R. Superfine, "Bending and buckling of carbon nanotubes under large strain," *Nature* **389**, 582–584 (1997).
- ³R. S. Lee, H. J. Kim, J. E. Fischer, A. Thess, and R. E. Smalley, Conductivity enhancement in single-walled carbon nanotube bundles doped with K and Br, *Nature* **388**, 255–257 (1997).
- ⁴P. G. Collins and P. Avouris, "Nanotubes for electronics," *Sci. Am.* **283**, 62–69 (2000).
- ⁵E. T. Thostenson, Z. Ren, and T.-W. Chou, "Advances in the science and technology of carbon nanotubes and their composites: A review," *Compos. Sci. Technol.* **61**, 1899–1912 (2001).
- ⁶W. A. de Heer, A. Chatelain, and D. Ugarte, "A carbon nanotube field-emission electron source," *Science* **270**, 1179–1180 (1995).
- ⁷H. Dai, J. H. Hafner, A. G. Rinzler, D. T. Colbert, and R. E. Smalley, "Nanotubes as nanoprobe in scanning probe microscopy," *Nature* **384**, 147–150 (1996).
- ⁸R. Martel, T. Schmidt, H. R. Shea, T. Hertel, and P. Avouris, "Single- and multi-wall carbon nanotube field-effect transistors," *Appl. Phys. Lett.* **73**, 2447–2449 (1998).
- ⁹W. B. Choi *et al.*, "Fully sealed, high-brightness carbon-nanotube field-emission display," *Appl. Phys. Lett.* **75**, 3129–3131 (1999).
- ¹⁰J. Kong *et al.*, "Nanotube molecular wires as chemical sensors," *Science* **287**, 622–625 (2000).
- ¹¹R. H. Baughman, A. A. Zakhidov, and W. A. de Heer, "Carbon nanotubes—The route toward applications," *Science* **297**, 787–792 (2002).
- ¹²A. Javey, J. Guo, Q. Wang, M. Lundstrom, and H. Dai, "Ballistic carbon nanotube field-effect transistors," *Nature* **424**, 654–657 (2003).
- ¹³A. Modi, N. Koratkar, E. Lass, B. Wei, and P. M. Ajayan, "Miniaturized gas ionization sensors using carbon nanotubes," *Nature* **424**, 171–174 (2003).
- ¹⁴J. Robertson, "Realistic applications of CNTs," *Mater. Today* **7**, 46–52 (2004).
- ¹⁵W. I. Milne *et al.*, "Carbon nanotubes as field emission sources," *J. Mater. Chem.* **14**, 933–943 (2004).
- ¹⁶M. W. Rowell *et al.*, "Organic solar cells with carbon nanotube network electrodes," *Appl. Phys. Lett.* **88**, 233506 (2006).
- ¹⁷A. Naeemi and J. D. Meindl, Carbon nanotube interconnects, *Annu. Rev. Mater. Res.* **39**, 255–275 (2009).

- ¹⁸H. Park *et al.*, "High-density integration of carbon nanotubes via chemical self-assembly," *Nat. Nanotechnol.* **7**, 787–791 (2012).
- ¹⁹M. M. Shulaker *et al.*, "Carbon nanotube computer" *Nature* **501**, 526–530 (2013).
- ²⁰P. L. Walker, J. F. Rakszawski, and G. R. Imperial, "Carbon mixture over iron catalysts. II. Rates of carbon formation," *J. Phys. Chem.* **63**, 140–149 (1959).
- ²¹P. A. Tesner, E. Y. Robinovich, I. S. Rafalkes, and E. F. Arefieva, "Formation of carbon fibers from acetylene," *Carbon* **8**, 435–442 (1970).
- ²²R. T. K. Baker, M. A. Barber, P. S. Harris, F. S. Feates, and R. J. Waite, "Nucleation and growth of carbon deposits from the nickel catalyzed decomposition of acetylene," *J. Catal.* **26**, 51–62 (1972).
- ²³G. G. Tibbetts, "Why are carbon filaments tubular?," *J. Cryst. Growth* **66**, 632–638 (1984).
- ²⁴A. Oberlin, M. Endo, and T. Koyama, "Filamentous growth of carbon through benzene decomposition," *J. Cryst. Growth* **32**, 335–349 (1976).
- ²⁵D. S. Bethune *et al.*, "Cobalt-catalyzed growth of carbon nanotubes with single-atomic-layer walls," *Nature* **363**, 605–607 (1993).
- ²⁶T. Guo *et al.*, "Self-assembly of tubular fullerenes," *J. Phys. Chem.* **99**, 10694–10697 (1995).
- ²⁷T. Guo, P. Nikolaev, A. Thess, D. T. Colbert, and R. E. Smalley, "Catalytic growth of single-walled nanotubes by laser vaporization," *Chem. Phys. Lett.* **243**, 49–54 (1995).
- ²⁸A. A. Puretzky *et al.*, "Investigations of single-wall carbon nanotube growth by time-restricted laser vaporization," *Phys. Rev. B* **65**, 245425 (2002).
- ²⁹A.-C. Dupuis, "The catalyst in the CCVD of carbon nanotubes—A review," *Prog. Mater. Sci.* **50**, 929–961 (2005).
- ³⁰M. Kumar and Y. Ando, "Chemical vapor deposition of carbon nanotubes: A review on growth mechanism and mass production," *J. Nanosci. Nanotechnol.* **10**, 3739–3758 (2010).
- ³¹M. José-Yacamán, M. Miki-Yoshida, L. Rendón, and J. G. Santiesteban, "Catalytic growth of carbon microtubules with fullerene structure," *Appl. Phys. Lett.* **62**, 657–659 (1993).
- ³²W. Z. Li *et al.*, "Large-scale synthesis of aligned carbon nanotubes," *Science* **274**, 1701–1703 (1996).
- ³³Y. C. Choi *et al.*, "Controlling the diameter, growth rate, and density of vertically aligned carbon nanotubes synthesized by microwave plasma-enhanced chemical vapor deposition," *Appl. Phys. Lett.* **76**, 2367–2369 (2000).
- ³⁴Y. Li *et al.*, "Growth of single-walled carbon nanotubes from discrete catalytic nanoparticles of various sizes," *J. Phys. Chem. B* **105**, 11424–11431 (2001).
- ³⁵E. F. Kukovitsky, S. G. L'vov, N. A. Sainov, V. A. Shustov, and L. A. Chernozatonskii, "Correlation between metal catalyst particle size and carbon nanotube growth," *Chem. Phys. Lett.* **355**, 497–503 (2002).
- ³⁶Y. Wei, G. Eres, V. I. Merkulov, and D. H. Lowndes, "Effect of catalyst film thickness on carbon nanotube growth by selective area chemical vapor deposition," *Appl. Phys. Lett.* **78**, 1394–1396 (2001).
- ³⁷S. Hofmann *et al.*, "Effects of catalyst film thickness on plasma-enhanced carbon nanotube growth," *J. Appl. Phys.* **98**, 034308 (2005).
- ³⁸Z. P. Huang *et al.*, "Growth of highly oriented carbon nanotubes by plasma-enhanced hot filament chemical vapor deposition," *Appl. Phys. Lett.* **73**, 3845–3847 (1998).
- ³⁹M. Meyyappan, "A review of plasma enhanced chemical vapour deposition of carbon nanotubes," *J. Phys. D: Appl. Phys.* **42**, 213001 (2009).
- ⁴⁰D. Narducci, L. Toselli, and P. Milani, "Modeling of aerosol-assisted chemical vapor co-deposition of NiO and carbon nanotubes," *J. Phys. IV* **09**, Pr8-741–Pr8-747 (1999).
- ⁴¹K. Hernadi, A. Fonseca, J. B. Nagy, D. Bernaerts, and A. A. Lucas, "Fe-catalyzed carbon nanotube formation," *Carbon* **34**, 1249–1257 (1996).
- ⁴²D. Venegoni *et al.*, "Parametric study for the growth of carbon nanotubes by catalytic chemical vapor deposition in a fluidized bed reactor," *Carbon* **40**, 1799–1807 (2002).
- ⁴³H. Kanzow, A. Schmalz, and A. Ding, "Laser-assisted production of multi-walled carbon nanotubes from acetylene," *Chem. Phys. Lett.* **295**, 525–530 (1998).
- ⁴⁴N. Grobert *et al.*, "A novel route to aligned nanotubes and nanofibers using laser-patterned catalytic substrates," *Appl. Phys. A: Mater. Sci. Process.* **70**, 175–183 (2000).
- ⁴⁵M. H. Rummeli *et al.*, "Synthesis of single wall carbon nanotubes with invariant diameters using a modified laser assisted chemical vapour deposition route," *Nanotechnology* **17**, 5469–5473 (2006).
- ⁴⁶M. Löffler *et al.*, "On the formation of single-walled carbon nanotubes in pulsed-laser-assisted chemical vapor deposition," *Chem. Mater.* **20**, 128–134 (2007).
- ⁴⁷K. Maehashi, Y. Ohno, K. Inoue, and K. Matsumoto, "Chirality selection of single-walled carbon nanotubes by laser resonance chirality selection method," *Appl. Phys. Lett.* **85**, 858–860 (2004).
- ⁴⁸K. Sakai, S. Doi, N. Iwata, H. Yajima, and H. Yamamoto, "Growth position and chirality control of single-walled carbon nanotubes," *IEICE Trans. Electron.* **E94C**, 1861–1866 (2011).
- ⁴⁹M. Mahjouri-Samani *et al.*, "Laser induced selective removal of metallic carbon nanotubes," *Nanotechnology* **20**, 495202 (2009).
- ⁵⁰J.-P. Tessonnier and D. S. Su, "Recent progress on the growth mechanism of carbon nanotubes: A review," *ChemSusChem* **4**, 824–847 (2011).
- ⁵¹K. Zimmer, R. Böhme, and B. Rauschenbach, "Local growth of aligned carbon nanotubes at surface sites irradiated by pulsed laser," *Physica E* **40**, 2223–2226 (2008).
- ⁵²J. Kong, H. T. Soh, A. M. Cassell, C. F. Quate, and H. Dai, "Synthesis of individual single-walled carbon nanotubes on patterned silicon wafers," *Nature* **395**, 878–881 (1998).
- ⁵³S. Fan *et al.*, "Self-oriented regular arrays of carbon nanotubes and their field emission properties," *Science* **283**, 512–514 (1999).
- ⁵⁴K. B. K. Teo *et al.*, "Uniform patterned growth of carbon nanotubes without surface carbon," *Appl. Phys. Lett.* **79**, 1534–1536 (2001).
- ⁵⁵S. Hofmann *et al.*, "Catalyst patterning methods for surface-bound chemical vapor deposition of carbon nanotubes," *Appl. Phys. A: Mater. Sci. Process.* **81**, 1559–1567 (2005).
- ⁵⁶F. Xu, X. Liu, and S. D. Tse, "Synthesis of carbon nanotubes on metal alloy substrates with voltage bias in methane inverse diffusion flames," *Carbon* **44**, 570–577 (2006).
- ⁵⁷O. Englander, D. Christensen, and L. Lin, "Local synthesis of silicon nanowires and carbon nanotubes on microbridges," *Appl. Phys. Lett.* **82**, 4797–4799 (2003).
- ⁵⁸S. Dittmer, O. A. Nerushev, and E. E. B. Campbell, "Low ambient temperature CVD growth of carbon nanotubes," *Appl. Phys. A: Mater. Sci. Process.* **84**, 243–246 (2006).
- ⁵⁹D. S. Engström, N. L. Rupesinghe, K. B. K. Teo, W. I. Milne, and P. Bøgild, "Vertically aligned CNT growth on a microfabricated silicon heater with integrated temperature control—Determination of the activation energy from a continuous thermal gradient," *J. Micromech. Microeng.* **21**, 015004 (2011).
- ⁶⁰T. Xu, J. Miao, H. Li, and Z. Wang, "Local synthesis of aligned carbon nanotube bundle arrays by using integrated micro-heaters for interconnect applications," *Nanotechnology* **20**, 295303 (2009).
- ⁶¹M. S. Haque *et al.*, "On-chip deposition of carbon nanotubes using CMOS microhotplates," *Nanotechnology* **19**, 025607 (2008).
- ⁶²B. D. Sosnowchik and L. Lin, "Rapid synthesis of carbon nanotubes via inductive heating," *Appl. Phys. Lett.* **89**, 193112 (2006).
- ⁶³B. D. Sosnowchik, L. Lin, and O. Englander, "Localized heating induced chemical vapor deposition for one-dimensional nanostructure synthesis," *J. Appl. Phys.* **107**, 051101 (2010).
- ⁶⁴D. Bäuerle, *Laser Processing and Chemistry* (Springer, Berlin, 2011).
- ⁶⁵O. Conde and A. J. Silvestre, "Laser-assisted deposition of thin films from photoexcited vapour phases," *Appl. Phys. A: Mater. Sci. Process.* **79**, 489–497 (2004).
- ⁶⁶T. F. Deutsch, D. J. Ehrlich, and R. M. Osgood, "Laser photodeposition of metal films with microscopic features," *Appl. Phys. Lett.* **35**, 175–177 (1979).
- ⁶⁷D. Bäuerle, "Laser chemical processing: An overview to the 30th anniversary," *Appl. Phys. A: Mater. Sci. Process.* **101**, 447–459 (2010).
- ⁶⁸C. P. Christensen and K. M. Lakin, "Chemical vapor deposition of silicon using a CO₂ laser," *Appl. Phys. Lett.* **32**, 254–256 (1978).
- ⁶⁹G. Leyendecker, D. Bäuerle, P. Geitner, and H. Lydtin, "Laser induced chemical vapor deposition of carbon," *Appl. Phys. Lett.* **39**, 921–923 (1981).
- ⁷⁰W. Kräuter, D. Bäuerle, and F. Fimberger, "Laser induced chemical vapor deposition of Ni by decomposition of Ni(CO)₄," *Appl. Phys. A: Mater. Sci. Process.* **31**, 13–18 (1983).
- ⁷¹M. S. Dresselhaus and P. C. Eklund, "Phonons in carbon nanotubes," *Adv. Phys.* **49**, 705–814 (2000).
- ⁷²M. S. Dresselhaus, G. Dresselhaus, R. Saito, and A. Jorio, "Raman spectroscopy of carbon nanotubes," *Phys. Rep.* **409**, 47–99 (2005).
- ⁷³R. Alexandrescu *et al.*, "Synthesis of carbon nanotubes by CO₂-laser-assisted chemical vapour deposition," *Infrared Phys. Technol.* **44**, 43–50 (2003).
- ⁷⁴F. Rohmund, R.-E. Morjan, G. Ledoux, F. Huisken, and R. Alexandrescu, "Carbon nanotube films grown by laser-assisted chemical vapor deposition," *J. Vac. Sci. Technol. B* **20**, 802 (2002).

- ⁷⁵V. Jourdain and C. Bichara, "Current understanding of the growth of carbon nanotubes in catalytic chemical vapour deposition," *Carbon* **58**, 2–39 (2013).
- ⁷⁶Z. Chen *et al.*, "Laser direct writing carbon nanotube arrays on transparent substrates," *Appl. Phys. Lett.* **90**, 133108 (2007).
- ⁷⁷J. B. Park, M. S. Jeong, and S. H. Jeong, "Direct writing of carbon nanotube patterns by laser-induced chemical vapor deposition on a transparent substrate," *Appl. Surf. Sci.* **255**, 4526–4530 (2009).
- ⁷⁸M. C. D. Bock *et al.*, "Optical feedback mechanisms in laser induced growth of carbon nanotube forests," *Appl. Phys. Lett.* **100**, 013112 (2012).
- ⁷⁹S. N. Bondi, W. J. Lackey, R. W. Johnson, X. Wang, and Z. L. Wang, "Laser assisted chemical vapor deposition synthesis of carbon nanotubes and their characterization," *Carbon* **44**, 1393–1403 (2006).
- ⁸⁰R. Longtin, L.-P. Carignan, C. Fauteux, D. Theriault, and J. Pegna, "Selective area synthesis of aligned carbon nanofibers by laser-assisted catalytic chemical vapor deposition," *Diamond Relat. Mater.* **16**, 1541–1549 (2007).
- ⁸¹R. Longtin, C. Fauteux, L.-P. Carignan, D. Theriault, and J. Pegna, "Laser-assisted synthesis of carbon nanofibers: From arrays to thin films and coatings," *Surf. Coat. Technol.* **202**, 2661–2669 (2008).
- ⁸²J. Shi *et al.*, "Synthesis of suspended carbon nanotubes on silicon inverse-opal structures by laser-assisted chemical vapour deposition," *Nanotechnology* **17**, 3822–3826 (2006).
- ⁸³S. Pisana *et al.*, "The role of precursor gases on the surface restructuring of catalyst films during carbon nanotube growth," *Physica E* **37**, 1–5 (2007).
- ⁸⁴G. D. Nessim *et al.*, "Tuning of vertically-aligned carbon nanotube diameter and areal density through catalyst pre-treatment," *Nano Lett.* **8**, 3587–3593 (2008).
- ⁸⁵G. D. Nessim *et al.*, "Precursor gas chemistry determines the crystallinity of carbon nanotubes synthesized at low temperature," *Carbon* **49**, 804–810 (2011).
- ⁸⁶I. Morjan *et al.*, "Carbon nanotubes growth from C₂H₂ and C₂H₄/NH₃ by catalytic LCVD on supported iron-carbon nanocomposites," *Physica E* **37**, 26–33 (2007).
- ⁸⁷I. Morjan *et al.*, "Carbon nanotubes grown by catalytic CO₂ laser-induced chemical vapor deposition on core-shell Fe/C composite nanoparticles," *Infrared Phys. Technol.* **51**, 186–197 (2008).
- ⁸⁸C. J. Lee and J. Park, "Growth model for bamboolike structured carbon nanotubes synthesized using thermal chemical vapor deposition," *J. Phys. Chem. B* **105**, 2365–2368 (2001).
- ⁸⁹K. Kwok and W. K. S. Chiu, "Growth of carbon nanotubes by open-air laser-induced chemical vapor deposition," *Carbon* **43**, 437–446 (2005).
- ⁹⁰S. Corthals *et al.*, "The beneficial effect of CO₂ in the low temperature synthesis of high quality carbon nanofibers and thin multiwalled carbon nanotubes from CH₄ over Ni catalysts," *Carbon* **50**, 372–384 (2012).
- ⁹¹Y. Fujiwara, K. Maehashi, Y. Ohno, K. Inoue, and K. Matsumoto, "Position-controlled growth of single-walled carbon nanotubes by laser-irradiated chemical vapor deposition," *Jpn. J. Appl. Phys., Part 1* **44**, 1581–1584 (2005).
- ⁹²K. Kasuya *et al.*, "Rapid and localized synthesis of single-walled carbon nanotubes on flat surface by laser-assisted chemical vapor deposition," *Jpn. J. Appl. Phys., Part 2* **46**, L333–L335 (2007).
- ⁹³J. B. Park *et al.*, "The rapid growth of vertically aligned carbon nanotubes using laser heating," *Nanotechnology* **20**, 185604 (2009).
- ⁹⁴J. B. Park, S. H. Jeong, and M. S. Jeong, "Position-controlled synthesis of single-walled carbon nanotubes on a transparent substrate by laser-induced chemical vapor deposition," *Appl. Surf. Sci.* **257**, 641–649 (2010).
- ⁹⁵S. Shang *et al.*, "Laser assisted direct write process with novel beam profiles," *Opt. Lasers Eng.* **51**, 527–532 (2013).
- ⁹⁶S. Chiashi, M. Kohno, Y. Takata, and S. Maruyama, "Localized synthesis of single-walled carbon nanotubes on silicon substrates by a laser heating catalytic CVD," *J. Phys.: Conf. Ser.* **59**, 155–158 (2007).
- ⁹⁷J. Shi *et al.*, "Direct synthesis of single-walled carbon nanotubes bridging metal electrodes by laser-assisted chemical vapor deposition," *Appl. Phys. Lett.* **89**, 083105 (2006).
- ⁹⁸M. Haluška *et al.*, "Time dependent growth of vertically aligned carbon nanotube forest using a laser activated catalytic CVD method," *Phys. Status Solidi B* **245**, 1927–1930 (2008).
- ⁹⁹M. Haluška, Y. Bellouard, Y. van de Burgt, and A. Dietzel, "In situ monitoring of single-wall carbon nanotube laser assisted growth," *Nanotechnology* **21**, 075602 (2010).
- ¹⁰⁰Y. van de Burgt, Y. Bellouard, R. Mandampambil, M. Haluška, and A. Dietzel, "Closed-loop control of laser assisted chemical vapor deposition growth of carbon nanotubes," *J. Appl. Phys.* **112**, 034904 (2012).
- ¹⁰¹Z. Liu *et al.*, "Pulsed laser CVD investigations of single-wall carbon nanotube growth dynamics," *Appl. Phys. A: Mater. Sci. Process.* **93**, 987–993 (2008).
- ¹⁰²T. Uchida and Y. Yoshida, "Development of a laser-assisted chemical vapor deposition system for the growth of carbon nanotubes," *J. Laser Micro/Nanoeng.* **6**, 214–219 (2011).
- ¹⁰³D. L. Jeanmaire and R. P. Van Duyne, "Surface Raman spectroelectrochemistry: Part I. Heterocyclic, aromatic, and aliphatic amines adsorbed on the anodized silver electrode," *J. Electroanal. Chem. Interfacial Electrochem.* **84**, 1–20 (1977).
- ¹⁰⁴L. Cao, D. N. Barsic, A. R. Guichard, and M. L. Brongersma, "Plasmon-assisted local temperature control to pattern individual semiconductor nanowires and carbon nanotubes," *Nano Lett.* **7**, 3523–3527 (2007).
- ¹⁰⁵W. H. Hung *et al.*, "Laser directed growth of carbon-based nanostructures by plasmon resonant chemical vapor deposition," *Nano Lett.* **8**, 3278–3282 (2008).
- ¹⁰⁶G. D. Nessim, "Properties, synthesis, and growth mechanisms of carbon nanotubes with special focus on thermal chemical vapor deposition," *Nanoscale* **2**, 1306–1323 (2010).
- ¹⁰⁷W. Xiong *et al.*, "Self-aligned growth of single-walled carbon nanotubes using optical near-field effects," *Nanotechnology* **20**, 025601 (2009).
- ¹⁰⁸M. Mahjouri-Samani *et al.*, "Diameter modulation by fast temperature control in laser-assisted chemical vapor deposition of single-walled carbon nanotubes," *Nanotechnology* **21**, 395601 (2010).
- ¹⁰⁹M. Balkanski, R. F. Wallis, and E. Haro, "Anharmonic effects in light scattering due to optical phonons in silicon," *Phys. Rev. B* **28**, 1928–1934 (1983).
- ¹¹⁰S. Chiashi, Y. Murakami, Y. Miyauchi, and S. Maruyama, "Temperature dependence of Raman scattering from single-walled carbon nanotubes: Undefined radial breathing mode peaks at high temperatures," *Jpn. J. Appl. Phys., Part 1* **47**, 2010–2015 (2008).
- ¹¹¹M. C. LeMieux *et al.*, "Self-sorted, aligned nanotube networks for thin-film transistors," *Science* **321**, 101–104 (2008).
- ¹¹²M. Ullmann, S. K. Friedlander, and A. Schmidt-Ott, "Nanoparticle formation by laser ablation," *J. Nanopart. Res.* **4**, 499–509 (2002).
- ¹¹³F. Dumitrache *et al.*, "Nearly monodispersed carbon coated iron nanoparticles for the catalytic growth of nanotubes/nanofibers," *Diamond Relat. Mater.* **13**, 362–370 (2004).
- ¹¹⁴E. R. Meshot *et al.*, "Engineering vertically aligned carbon nanotube growth by decoupled thermal treatment of precursor and catalyst," *ACS Nano* **3**, 2477–2486 (2009).
- ¹¹⁵J. B. In, C. P. Grigoropoulos, A. A. Chernov, and A. Noy, "Growth kinetics of vertically aligned carbon nanotube arrays in clean oxygen-free conditions," *ACS Nano* **5**, 9602–9610 (2011).
- ¹¹⁶D. B. Geohegan *et al.*, "In situ growth rate measurements and length control during chemical vapor deposition of vertically aligned multiwall carbon nanotubes," *Appl. Phys. Lett.* **83**, 1851–1853 (2003).
- ¹¹⁷A. A. Puzetzy, D. B. Geohegan, S. Jesse, I. N. Ivanov, and G. Eres, "In situ measurements and modeling of carbon nanotube array growth kinetics during chemical vapor deposition," *Appl. Phys. A: Mater. Sci. Process.* **81**, 223–240 (2005).
- ¹¹⁸Y. Avigal and R. Kalish, "Growth of aligned carbon nanotubes by biasing during growth," *Appl. Phys. Lett.* **78**, 2291–2293 (2001).
- ¹¹⁹Y. Zhang *et al.*, "Electric-field-directed growth of aligned single-walled carbon nanotubes," *Appl. Phys. Lett.* **79**, 3155–3157 (2001).
- ¹²⁰S. Huang, X. Cai, and J. Liu, "Growth of millimeter-long and horizontally aligned single-walled carbon nanotubes on flat substrates," *J. Am. Chem. Soc.* **125**, 5636–5637 (2003).
- ¹²¹M. Hofmann, D. Nezich, A. Reina, and J. Kong, "In-situ sample rotation as a tool to understand chemical vapor deposition growth of long aligned carbon nanotubes," *Nano Lett.* **8**, 4122–4127 (2008).
- ¹²²Y. S. Zhou *et al.*, "Laser-assisted nanofabrication of carbon nanostructures," *J. Laser Appl.* **24**, 042007 (2012).
- ¹²³W. Ruan, Z. Wang, J. Li, K. Jiang, and L. Liu, "Synthesis of carbon nanotubes on suspending microstructures by rapid local laser heating," *IEEE Sens. J.* **11**, 3424–3425 (2011).
- ¹²⁴Y. van de Burgt, A. Champion, and Y. Bellouard, "In-situ localized carbon nanotube growth inside partially sealed enclosures," *AIP Adv.* **3**, 092119 (2013).
- ¹²⁵J. B. Park *et al.*, "Fast growth of graphene patterns by laser direct writing," *Appl. Phys. Lett.* **98**, 123109 (2011).
- ¹²⁶J. B. Park *et al.*, "Transparent interconnections formed by rapid single-step fabrication of graphene patterns," *Appl. Phys. Lett.* **99**, 053103 (2011).
- ¹²⁷Y. van de Burgt, Y. Bellouard and R. Mandampambil, "Kinetics of Laser-Assisted Carbon Nanotube Growth," *Phys. Chem. Chem. Phys.* **16**, 5162–5173 (2014).