

# ***In situ* optical investigations into the nucleation and growth mechanism of carbon nanotubes**

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## **ABSTRACT**

We report hereby a temporally and spatially highly resolving optical measurement strategy, mainly based on linear Raman spectroscopy, with which it is possible to measure simultaneously and *in situ* the gas temperature and composition at different locations apart from the substrate surface as well as the structural quality of the growing carbon nanotubes (CNTs). In addition, the gas flow dynamics arising inside the reactor were characterized by particle image velocimetry (PIV). Thus, the correlations derived from these investigations can provide a sustained understanding of the CNTs nucleation and growth mechanism, which for the first time will consider experimentally the intermediate reaction steps taking place inside the reactor.

**Keywords:** catalytic chemical vapor deposition, carbon nanotubes, linear Raman spectroscopy, particle image velocimetry.

## **1 INTRODUCTION**

The attractive possibilities of using the outstanding properties of carbon nanotubes (CNTs) in a broad range of new applications have motivated substantial research effort in practically all fields of nanotechnology. However, the extensive use of these materials requires the development of scalable and selective formation processes; among them the catalytic chemical vapor deposition (CCVD) process is considered to be the most promising because of its simplicity, its low cost and the possibility of industrial scale-up due to the relatively low growth temperatures, high yields and high purities that can be achieved [1-4].

The CCVD process involves feeding a volatile precursor into a reactor containing one or more heated objects as substrates. Typically, transition metal nanoparticles are used to catalyze the thermal decomposition of the precursor leading to CNTs formation and growth [5]. Chemical reactions occur on the heated substrates and are accompanied by the production of exhaust by-products that leave the reactor together with residual reaction gases. Even though the formation and growth mechanisms of CNTs by CCVD have been extensively studied in the past, there is still no general

agreement about what the critical steps are and what the actual influence of the input parameters on the resulting structures is [6-9]. Therefore, the different processes taking place inside the reactor, such as mass and heat transport, chemical reactions in the gas phase and at surfaces as well as gas flow dynamics, should be investigated as a whole.

On this account, we propose a non-invasive, laser-based *in situ* measurement strategy that allows to analyze the intermediate processes in both gas and solid phases simultaneously, which take place inside the reactor and are not accounted for conventionally. Thus, this approach offers the possibility to establish correlations between the decomposition mechanism of the gaseous carbon source, the reaction conditions and the structure of the resulting CNTs. For its realization, measurement techniques like particle image velocimetry (PIV) and linear Raman spectroscopy (LRS) have been applied and incorporated into the CCVD system for the gas phase analysis whereas the measurement setup for the analysis of the solid phase is still being developed. Hence, we report here a comprehensive experimental study on the flow field and on the simultaneous determination of the gas composition and temperature via PIV and LRS, respectively, as well as the progress on the investigations carried out in the solid phase so far.

## **2 EXPERIMENTAL DETAILS**

### **2.1 CCVD system**

The CCVD system consists of a vertically oriented home-made cold wall flow reactor, which has been selected for the CCVD of CNTs due to its simplicity in operation [10, 11]. As shown in figure 1, the cold wall reactor is provided with optical access by four tubes in crosswise arrangement and the reactor windows are made out of high temperature-resistant quartz glass. The feed gas flow (usually composed of a carrier gas and a carbon source) without being pre-heated is introduced into the reactor at the bottom through an inlet pipe and the hot exhaust gases leave the reactor at the top through the gas exhaust pipe. Figure 1 shows also the inner part of the reactor, which consists of a resistive heating cartridge construction used to reach and maintain a well-defined substrate temperature. At its bottom, a square-shaped indentation is milled to serve as

placeholder for the substrate Si/SiO<sub>2</sub>-wafer where the CNTs are deposited. The heating cartridge construction is fixed to the upper reactor cap and it is controlled and supplied with electric power by a microprocessor temperature controller. Two NiCrNi-thermocouples (type K) are used to control and indicate the desired substrate temperature. The distance between the substrate surface and the inlet pipe can be varied by shifting the inlet pipe upwards and downwards.

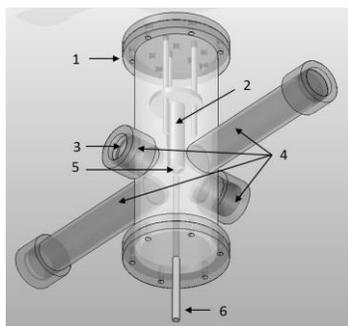


Figure 1: Optically accessible CCVD cold wall reactor. 1: upper reactor cap, 2: heating cartridge, 3: window, 4: optical access tubes, 5: substrate Si/SiO<sub>2</sub>-wafer, 6: inlet pipe.

## 2.2 Experimental details for the gas phase analysis

The regions of interest for the gas phase analysis are located between the inlet pipe and the substrate surface, where the CNTs are to be grown. So far, two different optical setups have been built up to study the gas flow dynamics via PIV and to determine the gas temperature and composition via LRS.

### 2.2.1 PIV optical setup

Since PIV is a measurement technique that computes the flow velocity field from patterns that can be extracted and correlated from subsequent illumination events of particles in a flow, most suitable particles have to be seeded to the gas flow. Since the aim hereby is to characterize the flow field inside the CCVD reactor, neither catalyst nor carbon source was used and consequently, no CNTs were formed. The feed flow was composed of pure nitrogen, as it is the typical carrier gas used for the CCVD of CNTs. The substrate temperature and operation pressure were kept constant at 953 K and 980 mbar, respectively. Further experimental details and information about the generation and supply of the seeded flow can be found elsewhere [12].

A schematic of the PIV optical setup is shown in figure 2. The scattering process is excited by a double-pulse Nd-YAG laser emitting two subsequent light pulses with an adjustable time delay at a wavelength of 532 nm. The two subsequent light pulses are emitted with a repetition rate of 10 Hz and each single laser pulse has 8 ns (FWHM) duration. By several mirrors, spherical lenses and a

cylindrical lens, a vertical laser light sheet with a height limited by the bore diameter of the windows is formed and focused through the central plane of the reactor. The light, which is elastically scattered from the particles, is detected perpendicularly to the laser light sheet. By means of a CCD-camera, which is operated in double-shutter mode, the signals generated by the two subsequent laser pulses are recorded two-dimensionally (2-D) and independent from each other, i.e. one image corresponds to one single excitation event. An external pulse generator is used to synchronize the laser pulses with the CCD-camera. The time delay between two consecutive laser pulses was chosen to be 100  $\mu$ s in order to acquire reliable images of the seeded flow for the PIV calculation. The calculation of the velocity distributions consisted in an average cross-correlation of twenty pairs of PIV raw images. More details about the detection system and the PIV evaluation method are reported elsewhere [12].

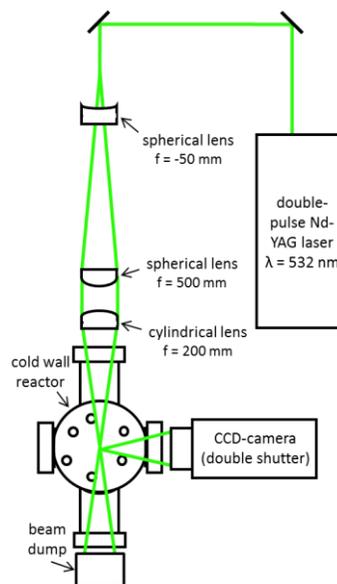


Figure 2: Schematic of the PIV optical setup used for the characterization of the flow field in the CCVD reactor.

### 2.2.2 LRS optical setup

Similarly to the execution of the PIV experiments, the CCVD process was operated at steady-state conditions, at atmospheric pressure and at a constant substrate temperature of 953 K. In this case, however, acetylene was added to the feed flow to take into account the effect of the carbon source, but any CNTs were formed, since any catalyst was used in the first instance.

The experimental LRS setup is shown in figure 3. The excitation source is a frequency-doubled Nd:YAG laser cluster, which is explained in detail elsewhere [13]. The laser cluster emits pulses of 8 ns (FWHM) duration with a repetition rate of 10 Hz and a single-pulse energy of 360 mJ at 532 nm. The laser pulse is temporally stretched in a single-loop pulse stretcher to reduce the pulse intensity and

by means of a plano-concave and a plano-convex lens the laser beam is expanded in order to decrease the fluence. By a further spherical lens, the laser beam is focused to the desired measurement location inside the CNT reactor. Perpendicularly to the laser propagation, the scattered light is collected and collimated with an achromatic lens. A long pass filter with high transmission for wavelengths longer than 535 nm is used to suppress the elastically scattered light. The Raman signals are transmitted and focused onto the entrance slit of a spectrometer ( $f = 250$  mm, 600 lines mm<sup>-1</sup>) by a second achromatic lens. The signals are detected with an electron multiplying charge-coupled device (EMCCD) camera with a quantum efficiency of more than 90 % in the detected spectral range. In order to increase the signal-to-noise ratio two measures were taken. On the one hand, the 400-pixel axis was binned completely to obtain an average spectrum of the 3.2 mm long probe volume and on the other hand, 200 single spectra were added together in computer memory to achieve an accumulated spectrum. The exposure time of the camera was set to the minimum possible value of 10  $\mu$ s in order to overcome the interfering black body radiation of the heating cartridge. More experimental details can be found elsewhere [14].

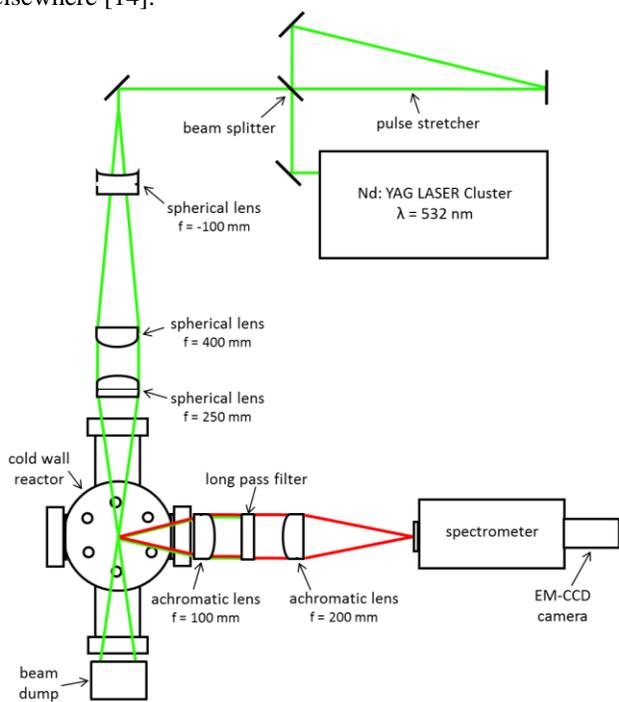


Figure 3: Schematic of the LRS setup for *in situ* gas composition and temperature measurements.

### 2.3 Experimental details for the solid phase analysis

For the experimental realization of the proposed measurement strategy, a concept of the complete optical setup that has to be incorporated into the CCVD system has

been conceived as it is shown in figure 4. Here, two different and independent LRS optical setups are needed for the excitation and acquisition of the Raman signals out of the gas and solid phases. Two of the optical accesses provided by the windows built in the reactor are used as excitation and detection pathways for the analysis of the gas phase (as mentioned in section 2.2) whereas the Raman signals out of the growing CNTs on the substrate surface are generated and collected (in backscattering direction) through an optical access located at the reactor bottom. For the detection of Raman spectra from the solid phase, a continuous wave (cw) laser beam is irradiated onto the substrate, where the CNTs are deposited. The resulting Raman signals are dispersed and collected in a spectrometer and a CCD-sensor, respectively with an exposure time of 100 ms. For the suppression of the elastic scattered light coming from the excited molecules and the reflections inside the reactor, a highly transmitting long pass filter with a steep edge is used. Hereby, the filtering of the Raman signals of interest as well as the protection of the CCD-sensor can be assured. A backscattering setup is preferred, as in this case the excitation and signal rays take exactly the same way to and from the measurement location. This means that in case of any thermally induced mechanical stress on the mechanical components, which might cause a shift of the excitation beam propagation path, the signal path will follow correspondingly and significant Raman spectra will still be detectable. Furthermore, the use of an optical fiber as a flexible light guide facilitates incorporating the setup for the solid phase analysis to the already existing setup for the gas phase analysis and the CCVD system.

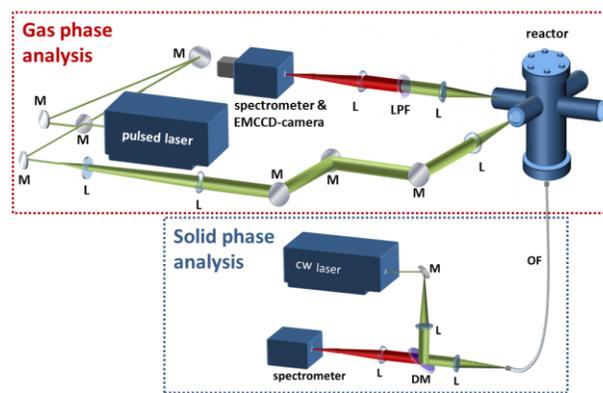


Figure 4: Concept of the LRS optical setups for the simultaneous *in situ* analysis of the gas and solid phase during the CCVD of CNTs. M: mirrors, L: lenses, LPF: long pass filter, DM: dichroic mirror, OF: optical fiber.

## 3 RESULTS

### 3.1 *In situ* analysis of the gas phase

PIV was applied to characterize the flow field in the vertically oriented CCVD cold wall reactor. Quantitative

information about the radial and axial profiles of the velocity components has been obtained and on their basis, actual volumetric flow rates, gas temperatures, the jet Reynolds number, the working regime as well as the residence time curves and the minimum impingement time of the feed flow into the substrate surface at different operation conditions were estimated. The reliability of the PIV measurements has been assessed with respect to the effect of the thermophoretic force, being partially compromised at defined regions attached to the substrate surface. These and further results are extensively reported elsewhere [12]. Figure 5 shows here exemplary one of the evaluated flow field velocity maps that arise between the substrate surface and the gas inlet pipe at CCVD operation conditions (85 mLn/min, 680°C, atm. pressure) as well as the location of the measurement positions for the gas phase analysis A, B and C. Locations A, B and C are not labeled as measurement points but as measurement lines of 3.2 mm length, as the Raman signals were integrated along these lines.

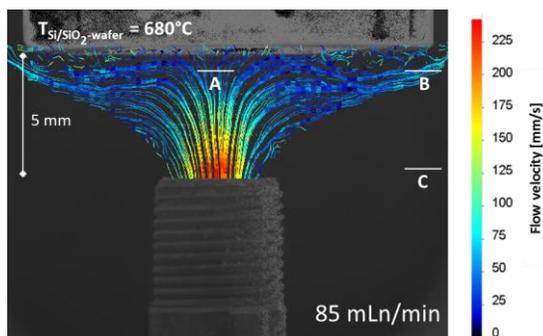


Figure 5: Flow field arising between the substrate surface and the gas inlet pipe at CCVD operation conditions and the location of the measurement positions in the gas phase A, B and C.

The simultaneous determination of the gas temperature and composition has been possible via a new approach for the evaluation of the Raman spectra and taking advantage of the feed gas flow composition. Figure 6 shows three Raman spectra, which were recorded from the gas phase inside the cold wall reactor at location A: i) at room temperature without acetylene (carbon source), ii) at CCVD temperature without acetylene, and iii) at CCVD temperature with addition of acetylene.

On the one hand, the temperature of the gas flow was evaluated by analyzing the peak integrals of the pure rotational Raman lines of hydrogen since they are known to be a function of temperature. On the other hand, the composition of the gas flow was determined by analyzing the peak integrals of the Stokes vibrational Raman Q-branches of the nitrogen and hydrogen molecules and of the C-C vibration band of acetylene since they are directly proportional to the number density of the respective molecules.

Table 1 summarizes some results from the simultaneous measurement of the gas temperature and acetylene conversion  $X_{C_2H_2}$  ( $= 1 - [c/c_0]$  where  $c$  and  $c_0$  are the acetylene concentrations in the measurement and in the inlet flow, respectively) at CCVD operation conditions.

Thus, for the first time to the best of our knowledge, linear Raman spectroscopy have been successfully applied to monitor *in situ* the gas phase at operation conditions favorable for the CCVD of CNTs [14].

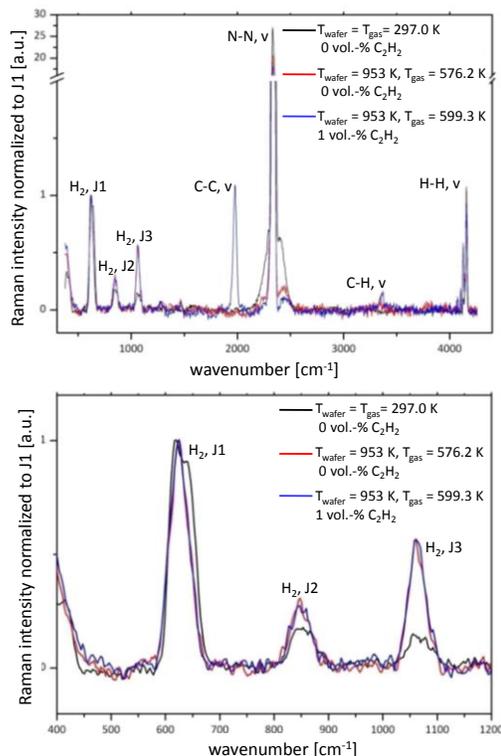


Figure 6: Raman spectra for the determination of the gas temperature and composition. Acquired under CCVD operation conditions at location A (see Fig. 5). (Top) Complete spectral range. (Bottom) Zoom-out of the rotational lines J1, J2 and J3 of hydrogen.

Location	$T_0$ (before $C_2H_2$ addition), [K]	$T_1$ (1 min after $C_2H_2$ addition), [K]	$X_{C_2H_2}$ (1 min after $C_2H_2$ addition), [%]
A	$576.2 \pm 10$	$599.3 \pm 17$	$31.8 \pm 2$
B	$867.0 \pm 22$	$1143.2 \pm 44$	$81.2 \pm 2$
C	$732.1 \pm 25$	$1285.4 \pm 49$	$82.5 \pm 2$

Table 1: Measured gas temperature and acetylene conversion  $X_{C_2H_2}$  at locations A, B and C before and after  $C_2H_2$  addition into the feed flow.

### 3.2 *In situ* analysis of the solid phase

The Raman signals to be detected out of the solid phase provide information about the microstructure and type of the deposited CNTs. Different Raman scattering modes are

expected to arise, some of first order, like the G-band ( $1580\text{ cm}^{-1}$ ) and the radial breathing mode (RBM) ( $75\text{-}300\text{ cm}^{-1}$ ) and some of second order, like the D- ( $1350\text{ cm}^{-1}$ ) and the D'-band ( $2700\text{ cm}^{-1}$ ). By considering ratios as D/G and G'/G, a measure of the average defectiveness level and smoothness degree can be determined, respectively. Information about a single-wall nanotube diameter can be obtained from the frequency of the RBM, since it is directly linked to its reciprocal [15].

First experiments with the optical setup shown in figure 4 have been carried out. As can be seen in figure 7, the characteristic G- and D-bands can be clearly observed but the  $\text{SiO}_2$ -peak, which is attributed to the Raman signal induced in the core of the applied optical fiber, represents here an interfering signal with the RBM spectral region. Possible solutions to overcome this problem are in progress now, like the implementation of a hollow silica waveguides and/or hollow-core fibers.

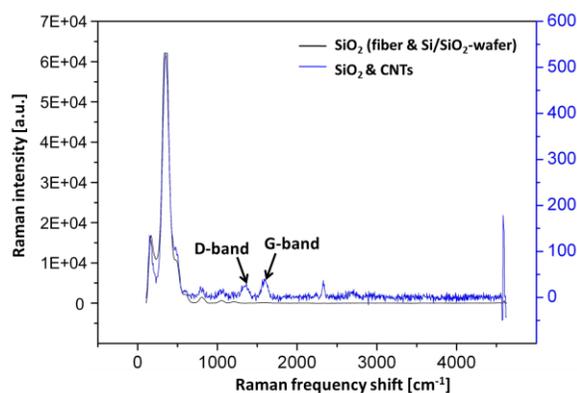


Figure 7: . Raman spectra acquired from the carbon microstructures formed by CCVD.

## 4 CONCLUSIONS

Through the implementation of the proposed *in situ* measurement strategy, it is possible to investigate simultaneously the gas and solid phase during the CCVD of CNTs and thus, take into account the effect of the reaction parameters on the reaction steps taking place inside the reactor and on the resulting carbon microstructures. Hence, this approach is capable to contribute to a better understanding on the CNTs formation and growth mechanism.

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