

IN-SITU MONITORING OF THE CATALYTIC CHEMICAL VAPOR DEPOSITION OF CARBON NANOTUBES

K. Reinhold-López¹, A. Schmitt¹, A. Braeuer¹, N. Popovska²
and A. Leipertz¹

¹ Lehrstuhl für Technische Thermodynamik and Erlangen Graduate School in Advanced Optical Technologies (SAOT), Universität Erlangen-Nürnberg, Germany

² Lehrstuhl für Chemische Reaktionstechnik, Universität Erlangen-Nürnberg, Germany

Introduction

The unique chemical and physical properties of carbon nanotubes (CNTs), which make them suitable for a wide range of applications, have stimulated interest for research since their discovery by Iijima in 1991 [1]. CNTs exhibit specific electronic properties and depending on their geometry, they can be either metallic or semiconducting [2]. In the field of mechanics, they are considered a potential composite material due to their extraordinary strength and low density. Additionally, CNTs are characterized by their high thermal stability up to 1400°C in vacuum [3-5]. Among the developed methods for growing CNTs, the catalytic chemical vapor deposition (CCVD) of hydrocarbon gases over a catalytic material turns out to be very promising because of its comparative simplicity, ease of control and low cost. Nevertheless, the CNTs nucleation and growth mechanism achieved by this method is not well understood yet.

The aim of this paper is to monitor the gas phase under typical CCVD operation conditions and thereby, to contribute to a better understanding of the process. Via particle image velocimetry (PIV) measurements, the impingement of the incident flow onto the hot substrate surface is characterized by determining the flow field. Through linear Raman scattering experiments, it is possible to measure simultaneously the acetylene (C-source) conversion as well as the temperature progress as a function of time. Thus, this concept offers the possibility to establish correlations between the decomposition mechanism, reaction conditions and the structure of the resulting CNTs.

Experimental

The CCVD process is carried out in a specially designed cold wall flow reactor with optical access to the substrate surface from several sides. The gas flow enters the reactor from the bottom through a pipe nearly at room temperature and impinges onto the hot substrate surface, which is a Si-wafer coated with iron nanoparticles whereon the CNTs are grown.

The experimental setups for the PIV and Raman measurements are shown in Fig. 1. Both scattering processes are excited by a pulsed frequency-doubled Nd-YAG laser at a wavelength of 532 nm with a repetition rate of 10 Hz and a pulse width of 10 ns (FWHM). By several mirrors, plano-

concave and convex lenses, the laser beam is focused into the center of reactor either as a light sheet for the PIV measurements or as a point for the Raman experiments. In order to obtain a better local resolution, the laser beam was expanded through a telescope. The detection side of both setups is arranged perpendicularly to the laser propagation. For the PIV measurements, a double shutter CCD camera is used to detect the light scattered by the seeded flow two-dimensionally (2-D). For the Raman scattering experiments, the Raman signal is imaged onto the slit of a spectrometer by means of the lenses L4 and L5 shown in Fig. 1b. The long pass filter LPF is used to suppress the elastically scattered light at 532 nm. The Raman signals are dispersed by a spectrometer and detected with an EMCCD camera of peak quantum efficiency up to 95%.

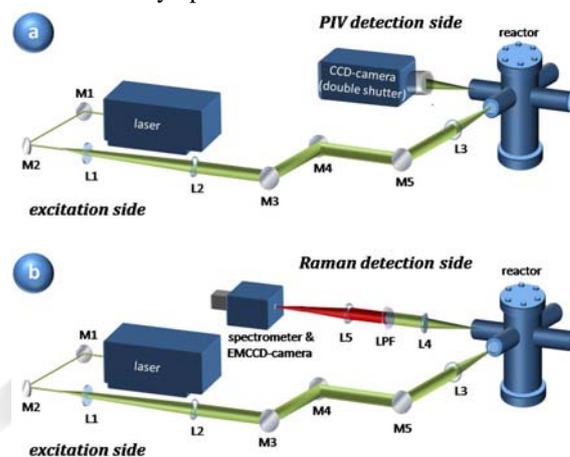


Fig. 1 Optical setups for the a) PIV and b) Raman scattering measurements. M: mirrors, L: lenses, LPF: long pass filter.

The PIV experiments were carried out with nitrogen as carrier gas seeded with particles of Calcilit 1G (99% CaCO₃). For the Raman experiments the gas mixture was composed of nitrogen (97 vol.%), acetylene (1 vol.%) and hydrogen (2 vol.%). Each Raman spectrum was taken with an exposure time of 10 μs and 200 accumulations. The operation conditions for both PIV and Raman experiments were set constant at atmospheric pressure, a Si-wafer temperature of 680°C and a total gas flow rate of 85 mLn/min. The distance between the substrate surface and the gas inlet pipe was 5 mm.

Results and Discussion

Due to the large temperature difference between the incoming gas mixture, which is nearly at room temperature and the substrate surface, which is heated up to 680°C, pronounced gas flow and temperature profiles in this region are expected to arise. The analysis of these phenomena is very important in order to select the most suitable operation conditions for the CCVD of CNTs.

On the one hand, the flow analysis allows the determination of the gas flow velocities, particularly at the vicinity of the substrate surface as well as the visualization

that in fact the incoming flow impinges onto the Si-wafer surface. Through the analysis of the temperature field, on the other hand, one can assure that the gas mixture reaches a temperature level at which the carbon source can decompose favoring the CNTs growth.

An overlap of the flow and temperature fields arising between the substrate surface and the gas inlet pipe is shown in Fig. 2. The incoming flow is slowed down abruptly in direction to the hot substrate surface. Indeed, the location of the abrupt deceleration of the flow coincides with the location, in which the temperature suddenly increases (from 3 to 2 mm away from the substrate surface). This can be attributed to the increment of the residence time and thus, to the stronger heating of the gas as shown in Table 1.

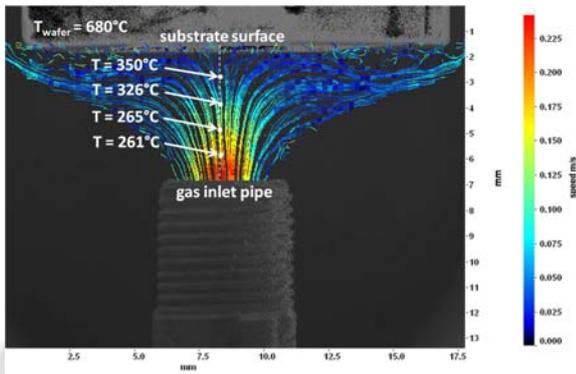


Fig. 2 Overlap of the flow and temperature fields arising between the substrate surface and the gas inlet pipe at CCVD operation conditions.

Table 1. Average velocities and residence times at different positions below the substrate surface

Position, mm	Temperature, °C	v, mm/s	τ , ms
1	350	50	154
2	326	80	120
3	265	180	60
4	261	200	50

Investigations monitoring the gas phase under CCVD conditions at 1 mm centrally below the substrate surface were carried out over time. Fig. 3 shows the progress of the gas temperature and acetylene conversion during 60 min.

The temperature progress indicates a nearly steady behavior since the gas temperature remains constant around 430°C. Tanzawa et al. [6] report that the thermal decomposition of acetylene can occur at temperatures ranging from 352°C to 3400°C. Thus, at the temperature level achieved, it is expected that certain amount of the incoming acetylene already decomposes. This expectation can be confirmed by looking at the progress of the acetylene conversion also shown in Fig. 3. We obtained that at 1 mm below the substrate surface around 30% of the incoming acetylene thermally decomposes.

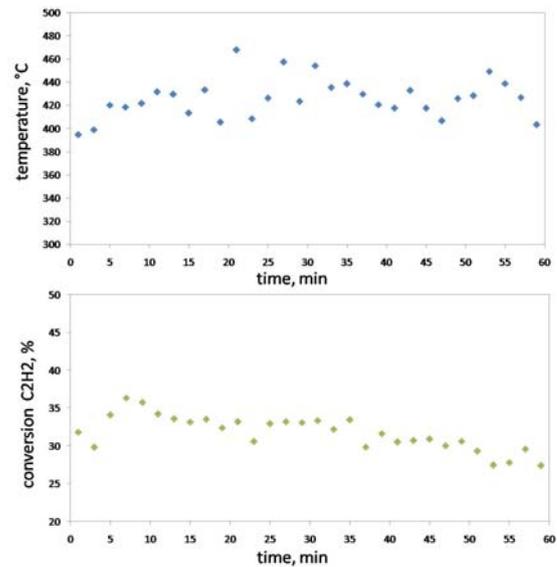


Fig. 3 Progress of the gas temperature and acetylene conversion over time.

Conclusions

Summarizing, through the implementation of the PIV and Raman measurement techniques, the impingement of the incident flow onto the hot substrate surface could be characterized. It was also possible to measure the acetylene conversion and the temperature progress of the gas phase as a function of time under CCVD operation conditions. Thus, the developed techniques are capable to contribute to a better understanding of the CNTs growth mechanism by offering the possibility to establish correlations between the decomposition mechanism, reaction conditions and the structure of the resulting CNTs.

Acknowledgments. The authors gratefully acknowledge financial support for parts of this work by the German Research Foundation (DFG) which additionally funds the Erlangen Graduate School in Advanced Optical Technologies (SAOT) in the framework of the German excellence initiative.

References

- [1] Iijima S. Helical microtubules of graphitic carbon. *Nature* 1991; 354(6348): 56-58.
- [2] Belin T, Epron F. Characterization methods of carbon nanotubes: a review. *Materials Science and Engineering B* 2005; 119(2): 105-118.
- [3] Teo KBK, Singh C, Chhowalla M, Milne WI. Catalytic synthesis of carbon nanotubes and nanofibers. *Encyclopedia of Nanoscience and Nanotechnology* 2003; 665-686.
- [4] Schmitt TC, Biris AS, Miller DW, Lupu D, Trigwell S, Rahman ZU. Analysis of effluent gases during the CCVD growth of multi-wall carbon nanotubes from acetylene. *Carbon* 2006; 44(10): 2032-2038.
- [5] Tans SJ, Verschuere ARM, Dekker C. Room-temperature transistor based on a single nanotube. *Nature* 1998; 393(6680): 49.
- [6] Tanzawa T, Gardiner WC. Reaction mechanism of the homogeneous thermal decomposition of acetylene. *J. Phys. Chem* 1980; 84: 236-239.