Nanocrystalline, high-surface-area silicon from gas-phase synthesis: A highly promising material for sustainable energy technology

Tim P. Hülser[1], Sophie M. Schnurre[1], Hartmut Wiggers[2], Christof Schulz[2]

[1]IUTA, Institute for Energy and Environmental Technology, 47229 Duisburg

[2]IVG, Institute for Combustion and Gasdynamics, University of Duisburg-Essen, 47048 Duisburg, Germany and
CeNIDE, Center for Nanointegration Duisburg-Essen, 47057 Duisburg

Introduction

Since decades, silicon is the leading material in microprocessor technology but its actual demand is driven by the photovoltaics industry that consumes about 80% of the high-purity silicon produced worldwide. The demand for silicon for solar cell applications has increased by about 350% from 2003 to 2010 [1] and driven a couple of technologies to provide a sufficient amount of high-purity solar-grade silicon. One of the cheap technologies providing high purity silicon is based on the gas-phase pyrolysis of monosilane SiH_4 and has been developed at the University of Duisburg-Essen [2]. As has been shown, this material exhibits nanostructured crystallinity as a result of its formation process in the gas phase .However, the specific properties of the nanostructure are lost when the material is used for the production of polycrystalline solar cells. As a result, highly promising properties of the nanostructured silicon generated via the gas-phase approach are not yet used in a wide variety of industrial, energy-related applications like photovoltaics [3], battery technology [4], or thermoelectrics [5]. This opens highly rewarding application fields in a rapidly growing market.

Polycrystalline silicon solar cells are manufactured from the as-prepared silicon powder from silane pyrolysis by re-melting and directional solidification. One of the main driving forces for the industrial utilization of the gas-phase pyrolysis of silane was the impressive energy balance with respect to alternative methods. The JSSI company claims, that the demand for electrical energy via this route can be reduced by about 90% compared to the conventional Siemens process based on chlorosilanes [6] requiring more than 200 kWh/kg silicon. However, commercial utilization of cheap, nanosized silicon is not foreseeable (yet).

In Li-ion batteries, the high storage capacity of lithium is well known and in principle enables the development of high-capacity anodes. However, strong mechanical stress related to a dramatic volume expansion and contraction during lithium storage and release causes *bulk silicon* to rapidly degrade, but *nanosized silicon* is believed to enable a sufficient long-term stability [4].

Nanostructuring of semi-metals is also known to be a highly promising path towards a profound improvement of the figure of merit of thermoelectrics. Nanostructuring of the thermoelectric material promotes phonon scattering leading to thermoelectrics with significantly reduced thermal conductivity but still high electric conductivity. With respect to the long lasting experience in silicon technology, silicon-based thermoelectrics made

from nanostructured raw material are highly rewarding materials with respect to sustainability and price. Two examples of the advantages of nanostructured silicon made from a continuously operating gas-phase synthesis process will be highlighted below.

Silicon nanoparticle synthesis

The silicon nanoparticles investigated in this work were produced in a hot-wall reactor (HWR) which is located in a pilot plant. Different process gases (sheath and carrier gases) and the precursor gases are injected at the top of the reactor. After precursor decomposition and particle formation in a hot zone, the particle-laden hot gases are pneumatically delivered to filtration. A pumping unit enabling a pressure range between 10 and 120 kPa and a thermal post-combustion system burning the off-gas from the pump are downstream the filters. The unit decomposes the gases (up to 200 l/min) at temperatures up to 1100°C.

The silicon particles were produced at different operating conditions varying the pressure range between 15 and 100 kPa and the temperature range between 800 and 1000°C. Typically, particles are formed at a precursor concentration of 10 vol% silane in a H_2/N_2 atmosphere. The resulting materials were analyzed with several techniques to investigate the relation between particle size, crystallinity, morphology, and synthesis conditions.

X-ray diffraction analysis (XRD) is used to analyze the influence of the synthesis conditions, especially the temperature, on the crystallinity. Figure 1shows the typical XRD patterns of nanoparticulate silicon synthesized at 800 and 1000°C, respectively. The broadening of the peaks is attributed to the nanocrystalline structure within the materials. The crystallite size was calculated using Scherrers' equation and it was found that silicon nanoparticles produced at 1000°C and 100 kPa consist of crystallites in the size regime of about 30 nm, while samples produced at lower pressure and/or lower temperature show smaller particle sizes. At 800°C, almost amorphous material is produced as indicated by the broad signals and the high background (see left graph in Figure 1). However, the positions and the intensity of the measured Bragg reflexes are in good agreement with the values found for bulk silicon and, therefore, prove the formation of silicon during the synthesis.
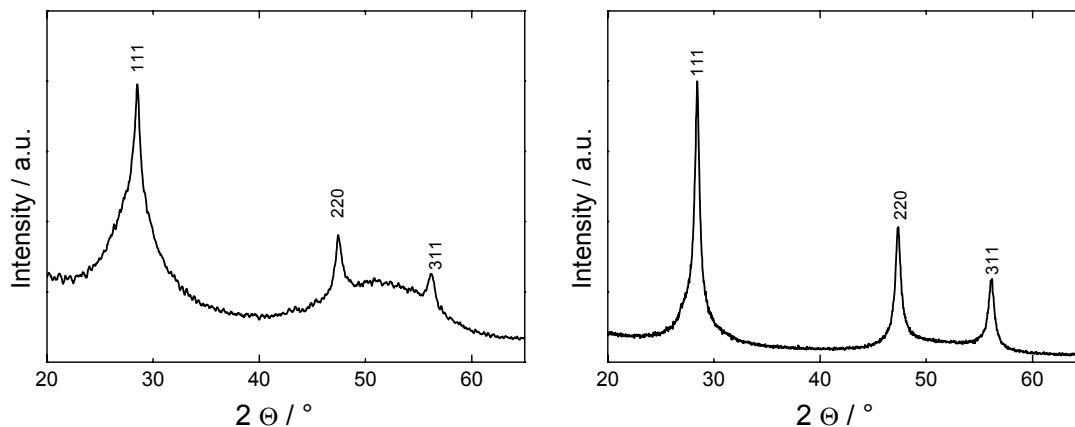
Figure 1: XRD patterns of silicon nanoparticles produced at 800 (left) and 1000°C (right). From the diffraction pattern it is obvious that the material synthesized at 800°C is almost amorphous while the silicon produced at 1000°C is crystalline.

Electron microscopy investigations were performed using transmission electron microscopy (TEM). Figure 2 shows a TEM micrograph of a typical sample of silicon nanoparticles from the hot-wall reactor. The particles always show a highly aggregated structure of smaller units (primary particles) with typical diameters smaller than 100 nm and distinct sintering necks to adjacent primary particles, while the overall aggregate size is much higher. Even the primary particles that form the large aggregates are polycrystalline as can be seen from the contrasts in Figure 2.
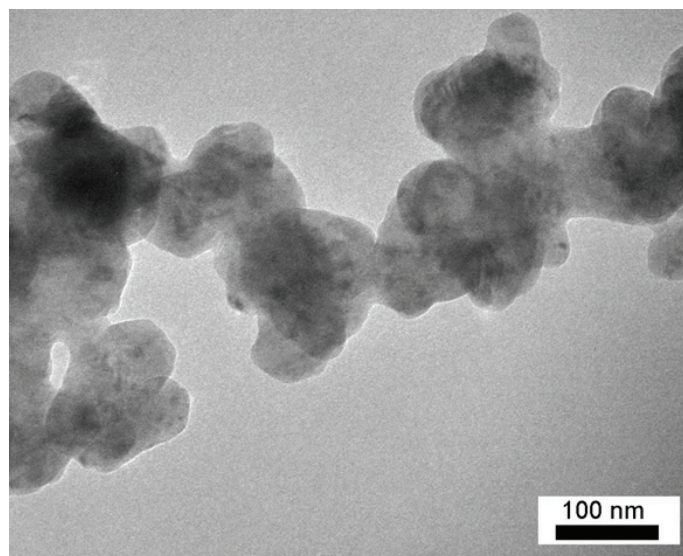

Figure 2: TEM Micrograph of aggregated Si nanoparticles from the HWR process.

Dispersibility and specific surface area were characterized using dynamic light scattering (DLS) and nitrogen adsorption according to Brunauer, Emmett and Teller (BET), respectively. For DLS, dispersions of silicon nanoparticles (synthesized at 1000°C) in acetone were produced using an ultrasonic bath for 1 hour at 200 W. Figure

3 shows the results of two representative materials. They reveal a decreasing mean particle diameter within the dispersion with decreasing process pressure. This typical finding is due to reduced aggregation of particles at lower pressures originating from reduced collision rates in the hot zone of the reactor.
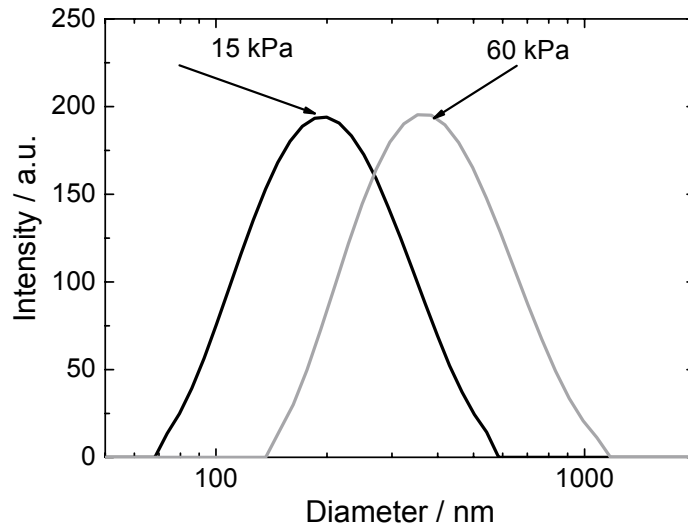

Figure 3: DLS measurement of silicon nanopowders dispersed in acetone produced at different pressures. The maxima of the normalized graphs indicate the mean particle size.

For BET analysis, silicon powders were taken from sealed product bags and analyzed after 24 h of outgassing under vacuum at 250°C. Figure 4 shows the specific surface area of silicon nanomaterials synthesized at 1000°C. The BET results show an increasing specific surface area with decreasing process pressure which can be attributed to the decreasing residence time in the hot zone of the reactor, as it is expected for gas-phase synthesis routes [7].
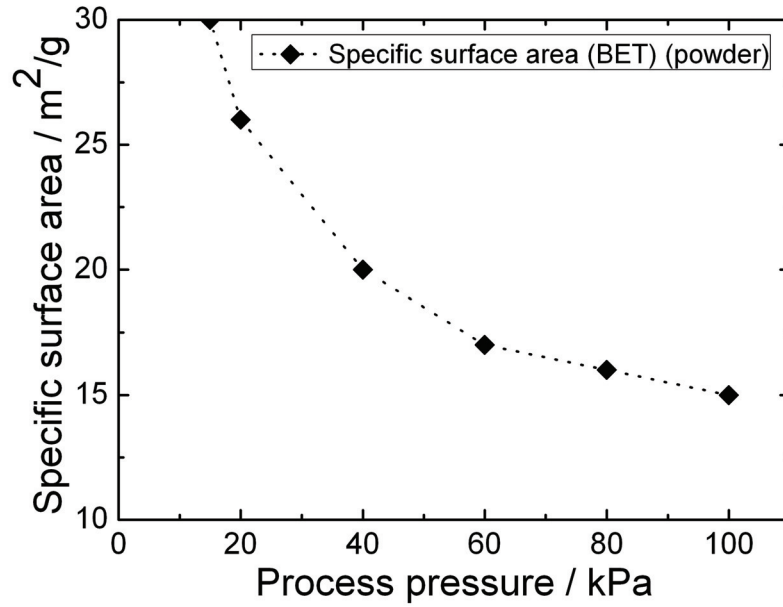
Figure 4: Specific surface area calculated from BET measurements on as-synthesized silicon nano-powder produced at different pressures.
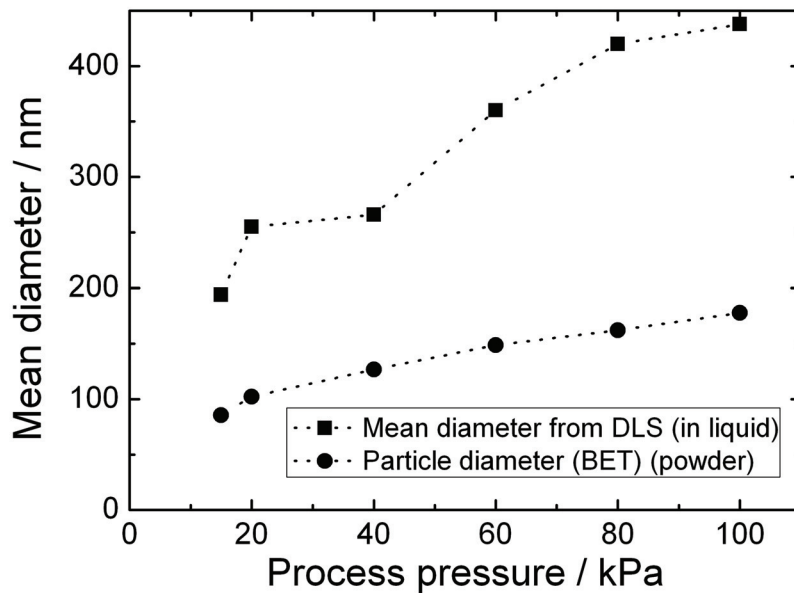

Figure 5: Mean particle-diameter determined from DLS and BET measurements on silicon nanomaterials produced at different pressures. The DLS investigation was performed in the liquid-phase (acetone) and BET measurements were done with the as-synthesized powder.

Figure 5 compares the mean particle diameter received from DLS measurements with those calculated from BET measurements assuming monodisperse, spherical particles. The difference between DLS and BET diameter increases with increasing pressure. This

5

obviously indicates that the agglomerate size increases due to higher collision rate and higher residence time.

To summarize the experimental findings of silicon nanoparticle synthesis: Depending on temperature, either almost amorphous (at lower temperature) or nanocrystalline (at higher temperature) silicon can be produced by pyrolysis of silicon in the gas phase. Typically, the materials consist of small, nanocrystalline or amorphous silicon building blocks that are sintered to primary particles with a typical size around 100 nm. These primary particles are found in TEM measurements, and BET investigations reveal a specific surface area that almost matches this result. Additionally, the primary particles form bigger, so-called hard agglomerates or aggregates, typically sizing slightly below 1 μm. These aggregates or hard agglomerates can be identified by DLS from liquid dispersions.

Nanocrystalline silicon for lithium-ion batteries

Silicon is known to exhibit a much higher storage capacity for lithium than the currently used graphite. Unfortunately, bulk silicon as well as microcrystalline silicon immediately decompose during the first few charge/discharge cycles, while nanocrystalline silicon shows significantly better performance.

To investigate the performance of our nanosized silicon for battery applications, silicon/graphite composite electrodes were prepared from silicon synthesized in the hot wall reactor at 1000°C. The electrodes were made of graphite, Super P as conducting agent, carboxymethylcellulose (CMC) as binder and 20 wt% silicon. The slurry was prepared by dispersing the mixture and then coated on a copper foil current collector.
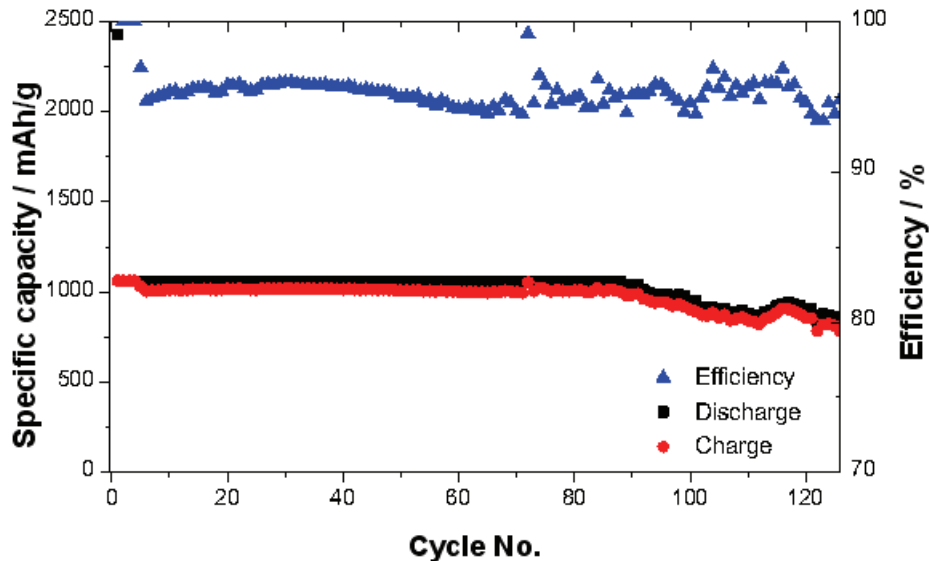

Figure 6: Cycling study of the graphite/silicon composite electrode.

The electrochemical behavior of our composite electrodes was tested by a cycling study (Figure 6) and the capacity was limited to 80% of the theoretical capacity. The results show that the composite electrode containing the nanocrystalline silicon can be processed for more than 120 full cycles with a slight degradation beginning after cycle 95 and an efficiency of about 95%. This is much better than reported for bulk- and microcrystalline silicon. Moreover, our results are very encouraging and among the best values found for silicon-containing electrodes.

Nanocrystalline silicon for thermoelectrics

Thermoelectric generators enable the direct transformation of thermal temperature gradient into electrical energy. Thermoelectrics are highly interesting for heat recovery, especially at high temperatures such as waste heat from processing plants or from automobile exhaust. Thermoelectric generators adapted to the exhaust of combustion engines can improve the fuel economy by conversion of waste heat to electric energy. One important route towards designing of thermoelectric generators with high efficiency is based on the decoupling of heat and charge transport by keeping high electrical conductivity and decreasing thermal conductivity. This is possible due to the fact that the mean free pathway of electrons is in the range of about 10 nm while that of phonons is in the range of 100 nm [8]. Grain boundaries as well as lattice mismatches are known for their efficient phonon scattering leading to a decreased thermal conductivity. As a result, scientists investigate to further enhance the efficiency of thermoelectric materials by introduction of artificial nanostructures to yield materials with a significantly lowered thermal conductivity due to phonon scattering.

Typical thermoelectric materials, however, use either toxic and rare (e.g., tellurium) raw materials. One important aim of the current development, is to use non-toxic raw materials with unlimited availability instead. Doped nanocrystalline silicon from the hot wall reactor can ensure high electric conductivity while its nanostructure should be able to decrease phonon transport. To test our materials, gas-phase synthesized silicon nanopowder doped with 1% of boron was spark-plasma sintered for 180 s at a temperature of 1100°C into almost dense pellets. The electrical conductivity σ, the thermal conductivity λ as well as the thermoelectric parameter, the Seebeck coefficient α were measured to determine the figure of merit ZT.
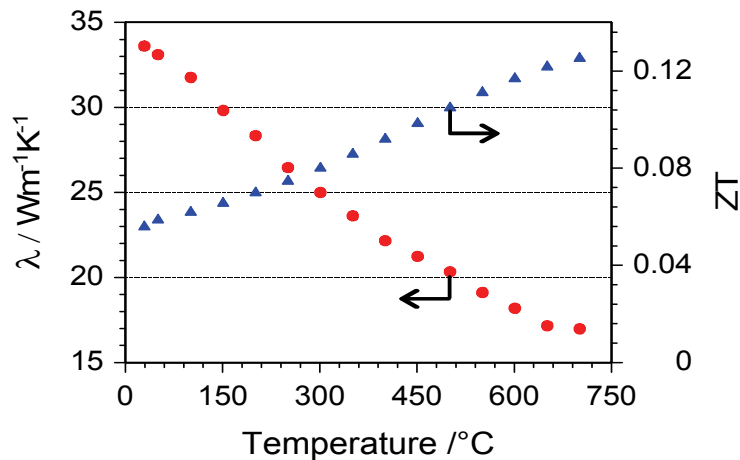

Figure 7: Thermal conductivity λ and figure of merit ZT of sintered, nanocrystalline, doped silicon from the hot-wall reactor.

Figure 7 shows the thermal conductivity λ and the figure of merit ZT of a sintered sample as a function of temperature. The thermal conductivity is significantly reduced compared to that of bulk silicon which is in the range of 140 $Wm^{-1}K^{-1}$. The measured data were also used to calculate the figure of merit *ZT*. The sample exhibits a value of ~0.125 at 750°C, which is slightly higher compared to silicon bulk materials. With respect to the early stage of our experiments on thermoelectrics from hot-wall reactor material we are confident that there is plenty of room for further improvement. Nanocrystalline silicon materials synthesized from a microwave plasma process show that the thermal conductivity can be further reduced by minimizing the crystallite size of the used silicon nanoparticles [9].

Summary

Gas-phase synthesis is a highly suitable method to mass produce nanostructured materials. The examples given in this paper, such as high-capacity Li-Ion-battery anodes and silicon-based thermoelectrics make use of this particular advantage. However, many other applications could profit from the tunable "nanoproperties" accessible via gas-phase synthesis.

References:
1. A.F.B. Braga; S.P. Moreira; P.R. Zampieri; J.M.G. Bacchin; P.R. Mei, Sol. Energy Mater. Sol. Cells 92 (2008) 418-424
2. H. Wiggers; R. Starke; P. Roth, Chem. Eng. Technol. 24 (2001) 261-264
3. M. Stupca; M. Alsalhi; T. Al Saud; A. Almuhanna; M.H. Nayfeh, Appl. Phys. Lett. 91 (2007) 063107
4. U. Kasavajjula; C.S. Wang; A.J. Appleby, J. Power Sources 163 (2007) 1003-1039
5. S.K. Bux; R.G. Blair; P.K. Gogna; H. Lee; G. Chen; M.S. Dresselhaus; R.B. Kaner; J.P. Fleurial, Adv. Funct. Mater. 19 (2009) 2445-2452
6. News, in: *elements Evonik Science Newsletter* 25 (2008) 11
7. C. Janzen; H. Kleinwechter; J. Knipping; H. Wiggers; P. Roth, J. Aerosol. Sci. 33 (2002) 833-841
8. L. Weber; E. Gmelin, Appl. Phys. A. 53 (1991) 136-140
9. N. Petermann; N. Stein; G. Schierning; R. Theissmann; B. Stoib; M.S. Brandt; C. Hecht; C. Schulz; H. Wiggers, J. Phys. D 44 (2011) 174034

See the following Strem Products discussed in this article

14-0650 Si- nanocrystalline

14-0655 Si- amorphous

Prof. Dr. Christof Schulz studied Chemistry at the University of Karlsruhe from 1988-94. He received his PhD at the Physical Chemistry Institute at the University of Heidelberg in 1997. From 1997-2004 he headed the group on "Laser diagnostics in combustion processes" in the same institute where he also received his Habilitation in 2002. During this time he was for several subsequent research periods at Stanford University, from 2000-02 as Visiting Scholar and from 2002-04 as Consulting Associate Professor. Since 2004 he directs the Institute for Combustion and Gasdynamics, IVG, at the University of Duisburg-Essen with a group of 45 scientists. His research focuses on reactive fluids with applications in combustion processes and nanomaterials synthesis. Elementary processes are studied in shock tubes and laser-diagnostics are developed and applied for in-situ measurements of concentrations and temperature. Processes are studied in well-controlled lab-scale devices as well as in optically accessible combustion engines and pilot-plant-scale reactors for materials synthesis with the aim to control processes based on a fundamental understanding. This expertise and the equipment available provides the capabilities to synthesizing a wide range of metal and metal oxide nanomaterials.

Prof. Schulz is the Director of CeNIDE, the Center for Nanointegration Duisburg-Essen, an organization with more than 50 participating Principal Investigators and their research groups in the field of nanoscience. He is also member of the Board of Directors of IUTA, The Institute for Energy and Environmental Technology in Duisburg.

Dr. Hartmut Wiggers graduated from Münster University in chemistry and received his PhD from Essen University. During his postgraduate research he was involved in the characterization of charge carrier transport processes in semi-conducting and quantum-sized materials. He is heading the nanomaterials group at the Institute for Combustion and Gas Dynamics at University Duisburg-Essen. His current research interests are the formation, chemistry and physics of crystalline, nanosized inorganic materials.

Dr. Sophie Marie Schnurre graduated from Clausthal University of Technology in mathematics and received her PhD at the Institute of Metallurgy at Clausthal University of Technology. After working several years as quality manager for an automotive supplier she went back to research and started as scientific assistant in the division "Conversion & Storage of Energy" at the Institute for Energy and Environmental Technology (IUTA) in Duisburg. Here she became project manager for the build up of the pilot plant facility and the new division "Nanomaterials Synthesis & Process Technology".

Tim Hülser graduated from Duisburg University in physics and worked afterwards for four years at the Institute for Combustion and Gasdynamics, IVG, at the University of Duisburg-Essen in the field of nanoparticle characterization and gas sensing properties of nanoparticulate semi-conducting materials. Then he moved to the Association of German Engineers (VDI) and worked as consultant in the field of future technologies with emphasis on wireless data transport and automotive applications. Currently he directs the division "Nanomaterials Synthesis & Process Technology" at the Institute of Energy and Environmental Technology, IUTA, where highly-specific nanoparticles are synthesized from the gas-phase on the pilot-plant scale.