Gas-Phase Synthesis of Nanoscale Silicon as an Economical Route Towards Sustainable Energy Technology

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Abstract

The silicon age that started in the 60s of the last century has changed the world profoundly, mainly related to the invention and development of microprocessor technology. Meanwhile, the demand for silicon is driven by the photovoltaics industry that consumes about 80% of the high-purity silicon produced worldwide. Independent of the final product, all high-purity silicon has passed through a couple of gas-phase reactions for purification. The most important gaseous species within this production chain are chlorosilanes and monosilane. We will discuss the direct formation of crystalline silicon by homogeneous gas-phase reactions as a direct and highly economical way to produce the required high-purity raw material for silicon solar cells. The direct formation of solid silicon particles from monosilane requires only a fraction of the energy compared to the established Siemens process based on the chemical vapor deposition of silanes. We have developed a method to synthesize nanocrystalline silicon powder using a hot-wall reactor, and the technology was scaled up to the pilot-plant scale. While an economical production strategy is decisive for solar cell production, the structure of the gas-phase product allows for additional, highly promising applications benefiting from the specific properties of the nanoscale particulate material. Both, thermoelectric generators as well as lithium-ion batteries benefit from the nanocrystalline structure of the gas-phase product due to high phonon scattering and short diffusion lengths, respectively. First successful examples with regard to these two topics will be discussed. In these fields, silicon finds potential new markets for sustainable energy technology because of its abundant availability and low-cost production.

Keywords: gas phase synthesis, silicon nanoparticles, pilot plant scale

Introduction

The demand for silicon for solar cell applications has increased by about 350% from 2003 to 2010 and has driven a couple of technologies to provide a sufficient amount of high-purity solar-grade silicon. Besides a couple of solid-state-based technologies such as the purification of metallurgical-grade silicon and the reaction of high-purity SiOx with high-purity carbon, the thermal decomposition of silicon-containing gaseous species is the established way to synthesize high-purity silicon from the gas phase. Common methods used in industry are based on the Wacker process, the ASiMi process, the MEMC process or the Hemlock HSC process. Multiple reports can be found dealing with the pyrolysis of monosilane (SiH4) as a precursor material. The homogeneous as well as heterogeneous decomposition of silane in free space and fluidized bed reactors was investigated intensely by Flagan et al. in the 1980s and several groups continued investigating silicon nanoparticle synthesis in free space reactors. One of these technologies was developed at the University of Duisburg-Essen and was scaled up to production scale. The description of silicon nanoparticle synthesis from monosilane in laboratory-sized reactors combined with the modeling of the process, i.e. reaction kinetics, nucleation and growth rates, thermodynamic driving force, particle size distributions and a comparison between experimentally obtained and
calculated particle size distributions was also investi-
gated by several authors. The modeling of nucle-
aulation, particle growth and particle size distribution in
different synthesis processes gained more and more
attention in order to predict or verify experimental
results. Furthermore, several reviews give an
account about the synthesis of silicon nanoparticles (SiNPs) from the vapor phase via non-thermal syn-
thesis routes, as well as from the thermal decompo-
sition of silanes.

The finding of Canham et al. that silicon nanocryst-
tals in the sub-10 nm regime exhibit visible lumines-
cence stimulated the development of new synthesis
strategies to produce free-standing, luminescing silicon nanoparticles from the gas phase with tunable size and small particle size distribution utilizing laser
or plasma pyrolysis of silane. The luminescing
properties of these materials are discussed with
respect to labeling or photosensitizer applications in
biological systems, and some investigations deal
with electronic applications based on silicon nanopar-
ticles such as memory devices, light emitters and
transistors. However, the production of narrow-
sized SiNPs in the sub-10 nm regime requires highly
diluted conditions of the silicon precursor leading to
clear production rates. In the context of this article,
we will focus on the economical formation of nano-
crystalline silicon and promising applications utiliz-
ing its nanocrystalline properties. Since the economi-
cal and energy-efficient formation of silicon involves
high precursor concentrations, applications requiring
small and luminescing SiNPs will not be covered.

One of the main driving forces for the industrial
utilization of silicon nanoparticle gas-phase synthe-
sis 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 con-
tentional Siemens process based on chlorosilanes
requiring more than 200 kWh/kg of silicon. The
as-prepared silicon powder from silane pyrolysis is used to
manufacture polycrystalline silicon solar cells by
re-melting and directional solidification.

As shown by several groups, silicon powder syn-
thesized by pyrolysis from monosilane exhibits a
nanostructured crystallinity as a result of its forma-
tion process in the gas phase, but 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 additional
properties of the nanostructured silicon generated in
this process are not yet being used in industrial
applications despite the fact that a technology for
the formation of such nanostructured materials is, in
principle, available. Nanostructured silicon has been
identified as an attractive material for a wide variety
of energy-related applications such as photovolta-
ics, battery technology or thermoelectrics. This
opens highly rewarding application fields in a
rapidly growing market.

In Li-ion batteries, the high storage capacity of
nanostructured silicon for lithium (10-fold increase
by weight compared to the state-of-the-art material
graphite) enables the development of high-capacity
anodes. However, a dramatic volume expansion and
contraction during lithium storage and release causes
bulk silicon to rapidly degrade. Nanosized silicon is
believed to enable a sufficient long-time stability.

Nanostructuring is also known to be one of the
key technologies for a profound improvement of the
figure of merit of thermoelectrics. The nanostructure
promotes phonon scattering, leading to materials
with highly reduced thermal conductivity while keeping
the electric conductivity high. Nanostructured,
silicon-based thermoelectrics are highly promising
with respect to sustainability and price. Silicon-based
materials can thus overcome one of the main hurdles
of the widespread application of thermoelectric de-
vices which is the limited availability of conventional
raw materials such as tellurium.

The challenge concerning the utilization of nano-
sized silicon is an economical and reproducible
approach toward tailor-made materials for specific
applications. While wet-chemical synthesis usually yields
surface-stabilized materials grown by thermodynamic
control, gas-phase processes allow for kinetic control
of the synthesis of high-purity nanoparticles. There-
fore, this method is especially favorable for the for-

mation of metastable materials such as highly-doped
nanoparticles and nanocomposites. Continuous gas-
phase processes have the additional advantage of
scalability to industrial production scale. In this paper
we discuss the path toward reasonable amounts of
highly specific silicon nanopowders that can be uti-
lized in thermoelectrics and lithium-ion batteries.

Pilot-plant facility

A multitude of highly specific nanomaterials have
been synthesized in specific lab-scale reactors in the
past. Typically, they are available in minute quanti-
ties only. Therefore, subsequent processing steps
cannot be studied and many nanomaterials have not
yet found their way into practical applications. To
make these materials available on the kg-scale, we designed a unique facility that combines three different synthesis routes via a hot-wall reactor (HWR), a flame reactor (FLR), and a plasma reactor (PLR) on the pilot-plant scale. In this work we will focus on silicon nanoparticles synthesized in the HWR which provides an efficient synthesis route with respect to the production rate and energy consumption of nanoscale silicon for a number of highly interesting application fields.

Detailed information about the kinetics of the gas-phase reactions of silane, particle formation and growth have been gathered from shock-tube and flow-reactor studies in the past\textsuperscript{10, 36}. These results have been incorporated into numerical models that were used to develop a flexible reactor system for the synthesis of nanocrystalline and amorphous silicon. The facility consists of a hot-wall reactor, a vacuum system, filter devices, a thermal post-combustion chamber for off-gases, and several in-situ and ex-situ analytic systems for process diagnostics. Fig. 1 shows a sketch of the three-level pilot-plant facility containing the HWR and the two additional reactors not used in the work reported here.

The hot-wall reactor is located on the third level of the pilot plant. Different process gases (sheath and carrier gases) and the precursor gases are injected at the top of the reactor via a multi-channel co-annular nozzle. After precursor decomposition and particle formation, the particle-laden hot gases are pneumatically delivered to the second level for filtration. The pumping unit which enables a pressure range between 10 and 120 kPa is located on the ground level, while the thermal post-combustion system for burning the off-gas of the pump is situated at an intermediate level above the pumps. The unit decomposes the gases (up to 200 l/min) at temperatures up to 1100 °C. Fig. 2 shows a photograph of the hot-wall reactor. The reactor is equipped with several ports that can be fitted with quartz windows to allow for optical in-situ diagnostics.

To enable operation of the HWR in continuous mode, a twin-filter system is installed. The particles are filtered alternately by one of the filter cartridges, while the other one can be freed from collected particles and prepared for further operation. Additionally, this double-filter system enables the separation of undefined particles that are generated in the first unsteady stages of production from those that are synthesized under the desired stable operating conditions. Such transient conditions occur after switching from inert gases to production gases due to changes in mass flow, heat capacity and temperature profile originating from the exothermic pyrolysis of silane. During the completely sealed bagging process, re-
verse pulsing is applied to blow the particles off the filter so that they drop into a bag mounted at the first level below the filter devices.

Diagnostics

On-line diagnostics

In recent years, laser diagnostics have proved to be very powerful for the in-situ analysis of combustion processes and have also transferred to the very promising high-temperature gas-phase synthesis of nanoparticles. Recent applications of high-temperature gas-phase particle synthesis are very promising. Consequently, the pilot plant is equipped with in-situ laser diagnostics and gas-analysis systems consisting of particle mass spectrometry and laser-induced incandescence (LII) set-ups that are available for monitoring the particle and aggregate size during different stages of the formation processes. These techniques enable on-line monitoring of the final particle size, which allows the products to be adjusted with different properties depending on the process conditions. On-line gas-phase analysis of the reactor exhaust is realized by a continuously operating quadrupole mass spectrometer (QMS, MKS microvision IP 300 D), to ensure the intended conversion of the precursor materials.

Off-line diagnostics

Scanning electron microscopy (SEM, LEO 1530) and transmission electron microscopy (TEM, Philips CM 12) are used to analyze the particle size and the state of agglomeration, while high-resolution transmission electron microscopy (HR-TEM, FEI Tecnai F20) is performed on selected materials to study details of the material structure. On-line and off-line results can be compared to specific surface area measurements, which were used to calculate mean particle sizes. The structure and crystallinity of the generated nanopowders are observed by X-ray diffraction (XRD, PANalytical XPert PRO). The crystallite size of multi-domain particle ensembles is then calculated using Scherrer’s equation.

Silicon nanoparticle synthesis

Process conditions

Silicon particles are produced in the HWR under various operating conditions. To investigate the influence of the synthesis pressure, particles are synthesized in the pressure range between 15 and 100 kPa and a temperature range from 800°C to 1000°C. Particles are formed with a precursor concentration of 10 vol% silane in a H₂/N₂ atmosphere at an initial total gas flow of 100 slm, resulting in 110 slm after decomposition of SiH₄. The precursor concentration of 10% SiH₄ allows for a production rate of 0.75 kg/h. With respect to the reactor geometry and assuming a constant process gas temperature of 1000°C within the reactor, a gas velocity of 0.7 m/s at 100 kPa and 4.8 m/s at 15 kPa is reached. Due to a highly sophisticated nozzle geometry with several coaxial gas flows that allow independent injection of sheath and diluent gases into the reactor, silane is kept away from the inner hot reactor walls. As a result, the heating and pyrolysis of silane takes place in the center of the reactor tube while chemical vapor deposition of silicon onto the inside of the reactor tube is prevented and stable operation without clogging is ensured for days. Therefore, material loss at the reactor walls is negligible.

Fig. 3 shows the gas velocities and the corresponding residence times for 900 and 1000°C at
various pressures at 1000°C. The open symbols refer to reaction conditions that lead to a complete conversion of SiH₄ as monitored by the analysis of filter off-gas via QMS. At 1000°C, complete conversion of silane is observed for all investigated pressures, while SiH₄ traces are found at 900°C at pressures lower than 80 kPa. Experiments at 800°C with a precursor concentration of 10% show incomplete conversion in the entire pressure range and therefore reduced production rates.

**Product analysis**

To investigate the relation between particle size, morphology and synthesis conditions, several techniques were applied to characterize several material properties. A Beckman Coulter Delsa™ Nano C was used to measure the size of dispersed silicon nanoparticles with dynamic light scattering (DLS), and the average particle diameters were experimentally determined from the specific surface area by the Brunauer-Emmett-Teller (BET) adsorption isotherm method assuming monodisperse, spherical particles with bulk density. For the DLS analysis, dispersions of silicon nanomaterial in acetone with 2.7 wt% were produced using an ultrasonic bath for one hour at 200 W. The overall volume of the dispersion was kept constant at 60 ml for the duration of sonication. **Fig. 4** shows a representative result of the DLS measurements. They reveal a decreasing mean particle diameter with decreasing process pressure, which is due to the reduced aggregation of particles at lower pressures originating from reduced collision rates in the hot zone of the reactor. For the BET analysis, silicon powders were taken from the sealed product bags and analyzed after 24 h of outgassing under vacuum at 250°C.

The BET results show an increasing specific surface area with decreasing process pressure due to the limited particle growth and decreasing residence time during synthesis, as is expected for gas-phase synthesis routes. **Fig. 5** compares the mean particle diameter received from DLS measurements with those calculated from BET measurements assuming monodisperse, spherical particles. The particle size increases with increasing process pressures as expected for the gas-phase synthesis route and as was also found for silicon particle formation. The particle size determined from the BET measurements is significantly smaller than that measured by DLS. This is attributed to the fact that the sintered particles exhibit a fractal structure with a dimension smaller than 3, leading to the typical open structure as it is commonly observed for materials from gas-phase synthesis. The discrepancy between the BET and DLS diameters increases with pressure, indicating a decreasing fractal dimension. TEM measurements affirm this result.

**Electron microscopy analysis**

Electron microscopy investigations are performed using HR-TEM, TEM and SEM. For the HR-TEM and TEM investigations, silicon powders were dis-
persed into acetone and sonicated for one hour at 200 W. The dispersion was dispensed on TEM grids and prepared for electron microscopy analysis. Fig. 6 shows a TEM micrograph of a typical sample of silicon nanoparticles from the hot-wall reactor. The particles show an aggregated structure of small units (primary particles) with diameters smaller than 100 nm. The overall aggregate size is in the same size regime as found in DLS measurements, while the smaller primary particles show faceting and distinct sintering necks to adjacent primary particles.

Primary particle size distributions were determined from aggregated primary particles with clearly visible sintering necks. From these analyses, size distributions with a geometric standard deviation $\sigma = 1.2$ to 1.3 are received, which is slightly lower than the expected value of 1.32 for a self-preserving particle size distribution in the continuum regime.
Even the primary particles that form the large aggregates are polycrystalline, as can be seen from the contrasts in Fig. 6 as well as from the HR-TEM bright field micrograph shown in Fig. 7a. The HR-TEM investigations reveal that the particles are polycrystalline with a high crystallinity throughout the particles, but also reveal a high defect density as stacking and twinning faults, which is obvious from the different shades of gray. The size of individual crystals is about 12 nm in diameter, which is significantly smaller than that of the primary particles. The images do not indicate the presence of an oxide shell on the particle surface, but due to handling in air, the highly reactive surface particles assumedly exhibit oxygen on the surface. Furthermore, a local enrichment of SiO₂ due to segregation areas in the particles is not observed. Therefore, the high defect density must be a result of lattice mismatches. Fig. 7a shows a HR-TEM micrograph of a Si particle and supports this assumption. It reveals the high crystallinity and also shows a couple of defects and stacking faults. Fig. 7b shows the border of the particle which proves the absence of an oxide layer on the particle surface, while Fig. 7c shows the Fourier transformation of the center image and underlines the polycrystallinity due to the appearance of closed rings in the illustration.

Fourier transform infrared (FT-IR) spectroscopy was applied to verify that the pristine particles are almost oxygen-free. Therefore, silicon nanopowder

![Fig. 6 TEM micrograph of aggregated Si nanoparticles from the HWR process at T = 1000°C and p = 300 mbar.](image)

![Fig. 7 HR-TEM images of a silicon nanoparticle. a) Core of the particle and lattice structure of the material. b) Border of the particle with the TEM grid, a distinctive oxide layer is not visible. c) Fourier transformation of the core area of the particle.](image)
samples were taken from the sealed bags and measured in diffuse reflectance mode using a Bruker IFS66v/S spectrometer under ambient conditions. As can be seen from Fig. 8, the FT-IR spectrum is dominated by the two strong signals at 630 cm\(^{-1}\) and 2100 cm\(^{-1}\) which are related to Si-H vibration modes\(^{48}\). Additionally, the typical signal found for the Si-O-Si stretching mode is observed around 1070 cm\(^{-1}\), and very small signals around 980 and 2250 cm\(^{-1}\) are found for vibrations of Si-H back-bonded to Si-O\(^{49}\). The signal at 1070 cm\(^{-1}\) is a highly sensitive proof for oxidation. From the fact that the intensities of the Si-H bands at 2100 cm\(^{-1}\) and 630 cm\(^{-1}\) are considerably large with respect to the Si-O-Si band at 1070 cm\(^{-1}\) (which exhibits a very high oscillatory strength), it can be deduced that the particle surfaces are only partially oxidized. This oxidation is most probably due to contact of the silicon nanopowder with air when removed from the sealed bag and during the FT-IR preparation procedure.

To analyze the influence of the synthesis temperature on the crystallite structure, XRD investigations were performed on selected samples. Fig. 9 shows two typical normalized XRD patterns of nanoparticulate silicon synthesized at 800 and 1000 °C. The vertical lines indicate the position of the Bragg maxima for bulk silicon. The broadening of the peaks is attributed to the nanocrystalline structure within the materials, and the crystallite size can be calculated from the patterns using the Scherrer equation:

\[
\Delta 2\Theta = \frac{0.89 \cdot \lambda}{B \cdot \cos \Theta}
\]  

For silicon nanoparticles produced at 1000 °C and 100 kPa, the crystallite size is in the regime of about 15 nm, while samples produced at 800 °C and 20 kPa reveal crystallite sizes of around 10 nm. From Rietveld analysis on the sample produced at lower temperatures, a crystalline quantity of about 8 vol% within the nanoparticulate powder is calculated. However, the positions of the measured Bragg reflexes are in good agreement with the values found for bulk silicon and, therefore, prove the formation of crystalline silicon during the synthesis.

The experimental set-up also allows for the production of doped materials. A homogeneous mixture of silane (SiH\(_4\), 10 vol%) and 0.02–3 vol% diborane/argon (2 vol% of diborane diluted in argon) was injected into the hot-wall reactor via the nozzle system. To visualize the effect of successful doping, two layers of doped and undoped silicon were prepared on one silicon wafer ready for SEM analysis utilizing the effect that brightness and contrast are different for similar materials with different conductivity, as described previously for different doped regions in silicon wafers\(^{50}\). Fig. 10 shows the two materials located next to each other, separated by a channel free of particles with the layer of undoped silicon on the left-hand side.
Fig. 9 XRD pattern of silicon nanoparticles produced at 800 and 1000°C. The vertical lines indicate the position of the Bragg maxima for bulk silicon.

Fig. 10 SEM investigation of layers of undoped silicon (left) and boron-doped (p-type) silicon (right). Brighter contrast is observed for undoped materials.
Despite their low overall performance, thermoelectric generators enable the direct transformation of thermal energy into electrical energy. Although thermoelectric properties of silicon from 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 sintered pellets were cut into blocks and the electrical conductivity $\sigma$, the thermal conductivity $\lambda$ as well as the thermoelectric parameter, the Seebeck coefficient $a$, were measured to determine the figure of merit $ZT$ using equation 2:

$$ZT = \frac{a^2 \sigma}{\lambda} T$$

**Fig. 11a** shows the thermal conductivity $\lambda$ versus temperature. The thermal conductivity decreases with increasing temperature and is significantly reduced compared to the thermal conductivity of bulk silicon which is in the range of 140 Wm$^{-1}$K$^{-1}$. 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$^{46}$. The results of the measurement are fit using a polynomial function to receive a continuous set of data for further processing. The calculated power factor (see **Fig. 11b**) increases slightly with increasing temperatures, which results from a higher absolute slope of the increasing Seebeck coefficient compared to the absolute value of the smaller slope of the decreasing electrical conductivity. The data are also fit using a polynomial function, and the polynomial function of both the thermal conductivity and the power factor are used to calculate the figure of merit $ZT$. **Fig. 11c** shows the figure of merit for nanostructured p-doped silicon pellets. The samples exhibit a maximum of $\sim$0.13 at 700°C, which is slightly higher compared to silicon bulk materials, and our most recent results of $ZT = 0.31$ at 700°C (not shown) demonstrate that there is plenty of room for further improvement.

The charge carrier concentration $n$ was calculated from the measured Seebeck coefficient as assumed for degenerated semiconductors$^{52,53}$:

$$n = \frac{\pi}{3} \left( \frac{C \cdot m^* \cdot T}{\alpha} \right)^{3/2} \text{ with } C = \frac{8\pi^2 k_B^2}{3e^2}$$

$m^*$ is the band effective mass, $k_B$ the Boltzmann and $h$ the Planck’s constant, and $e$ the charge of the electron. The calculated charge carrier concentration of $n=3.3 \times 10^{20}$ cm$^{-3}$ that is known to enable a maximum in $ZT^{62}$, and is very close to the normal doping concentration of $5 \times 10^{19}$ cm$^{-3}$. As a result, it can be stated that the gas phase approach is able to produce
raw materials for thermoelectrics with optimized morphology and electrical properties.

**Nanostructured silicon for lithium-ion batteries**

Electricity is a mainstay of today’s energy supply with increasing importance as it is easy to transfer for utilization in several different ways. Moreover, electrical energy storage is able to buffer fluctuating energy supply and use. It is obvious that energy storage is also of vital importance for mobile applications from laptops to electric vehicles, and an enormous demand for batteries with a high storage capacity and power density is predicted\(^{64}\). Especially the nanostructuring of materials and the synthesis of nanocomposites is a powerful way to meet the requirements of future electrical storage devices\(^{65}\).

New silicon/carbon nanocomposites for a multifold increase of the anode capacity of lithium-ion batteries are under development due to the fact that silicon is able to increase the storage capacity of presently used graphite dramatically. While the theoretical capacity of graphite (forming LiC\(_6\)) is quite poor (372 mAh/g), the silicon-based lithium intermetallic phase Li\(_{22}\)Si\(_5\) has a theoretical capacity of 4200 mAh/g\(^{32}\). Unfortunately, the high capacity is accompanied by extreme volume changes during lithium extraction and insertion of about 300%. Nanosized silicon particles are known to withstand the mechanical stress much better than bulk or micron-sized materials.

To investigate the ability of our nanosized silicon for battery applications, undoped silicon from the hot-wall reactor was used to prepare silicon/graphite composite electrodes. The electrodes were com-

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**Fig. 11** (a) Thermal conductivity $\lambda$, (b) power factor $\omega^2 \sigma$, and (c) figure of merit $ZT$ of nanocrystalline, boron-doped silicon from the hot-wall reactor.
posed of 60 wt% graphite, 20 wt% silicon, 12 wt% of the commercial carbon black additive "Super P®" as the conducting agent and 8 wt% carboxymethylcellulose (CMC) as the binder (see Fig. 12 right). The slurry was prepared by dispersing the mixture and it was then coated on a copper foil current collector.

The electrochemical behavior of the composite electrodes was tested by a cycling study shown in Fig. 13, and the capacity was limited to 80% of the theoretical capacity. The results show that the composite electrode can be processed for about 100 full cycles without significant degradation and an efficiency of about 95%. This result is very encouraging and among the best values ever reported in literature for silicon-containing electrodes.

**Process energy consumption**

The gas-phase synthesis of silicon nanoparticles from silane is a highly economical route for the generation of nanosized silicon. To determine the energy required to produce one kilogram of nanosilicon from monosilane (SiH₄), a standard test procedure was defined. The pressure was set to 100 kPa, which means that the process was carried out at atmospheric conditions. Therefore, the power consumption of the vacuum pumps can be neglected. The temperature in the reaction tube was set to 1000°C to ensure quantitative SiH₄ conversion and the sheath gas flow rate was kept constant at 120 slm, while the precursor flow rate was varied between 5 and 30 slm, which results in a corresponding precursor concentration of 4–20% by volume.

To allow for a uniform temperature throughout the entire hot-wall-reactor, the oven is separated into four heating zones. The current consumed by these heating zones was measured and used to calculate the demand for electrical energy to keep the hot-wall reactor at the given temperature for the different process conditions. The result of this calculation leads to a dimension for the total energy demand for the conversion of silane which is related only to the heating of the gases and heat losses, as the formation of silicon from silane is slightly exothermic:

\[
\text{SiH}_4(g) \rightarrow \text{Si(s)} + 2\text{H}_2, \Delta H = -34\text{kJ/mol} \quad (4)
\]

Fig. 14 shows the relation between the production rate (in kg/h) and the electrical energy required (in kJ/kg). It can be clearly seen that low production rates result in a comparatively high energy demand, decreasing with increasing production rate. The squares indicate the total energy required to run the reactor while the circles show the energy required to heat sheath and diluent gases to 1000°C (calculated from their heat capacity and mass flow). The difference between both values is mostly related to heat losses. As a result, it can be estimated that a hot-wall reactor with optimized insulation and waste heat recovery is able to produce silicon from SiH₄ with an energy requirement for the process that is below 5000 kJ/kg silicon (about 1.4 kWh/kg).

**Summary**

Gas-phase synthesis is a highly suitable method to mass-produce nanostructured materials. The merit of its key benefits can be best capitalized by keeping
and utilizing the specific properties that are due to its nanostructure. Applications that require high surface areas for energy and mass transport or a specific structure size are the highly promising application fields for such materials.

In this work, silicon particles are produced in a hot-wall reactor under various temperature and pressure conditions using silane as the precursor material. Boron doping of the silicon nanoparticles is realized using diborane as the precursor material. Production rates of up to 0.75 kg/h are received without losing the specifications of the material. The energy required to synthesize silicon materials from silane via the gas-phase route is found to be impressively low compared to established technologies based on the chemical vapor deposition of chlorosilanes. Full conversion rates of silane are claimed and the influence of gas velocity and residence time within the reactor on particle properties is investigated.

The resulting materials are characterized using several analytic methods. Both DLS and BET analysis prove an influence of the process pressure on

Fig. 13: Cycling study of the graphite/silicon composite electrode.

Fig. 14: Energy requirement for the production of a silicon nanomaterial from SiH₄ in the gas phase.
the granulated materials. DLS measurements demonstrate a decreasing agglomerate size, while the BET analysis shows an increasing specific surface area with decreasing process pressure. Electron microscopy demonstrates that the particles in the size regime smaller than 100 nm are sintered with distinctive sintering necks, as can be expected for a gas-phase synthesis process with high particle mass loading. Furthermore, HR-TEM analysis proves that these polycrystalline particles exhibit a high crystalline disorder but do not show a visible oxide layer on the particle surface, which is supported by FT-IR spectroscopy. XRD measurements substantiate the results received from HR-TEM investigation. The analysis method reveals a high crystallinity of the materials synthesized at $T = 1000^\circ$C and a high amorphous content in conjunction with small crystallites for lower temperatures ($T = 800^\circ$C).

The application examples given in this paper such as silicon-based thermoelectrics and high-capacity Li-ion battery anodes make use of the particular advantage that nanosized materials can yield with respect to sustainable energy technology.

In the field of thermoelectrics, first measurements of the figure of merit $ZT$ are presented which reveal promising $ZT$ values higher than 0.1 at temperatures of 800°C, and the calculated charge concentration confirms the successful incorporation of the dopant.

First investigations of the applicability of the nanocrystalline silicon for lithium-ion batteries are shown. The material is tested in silicon/graphite composite electrodes and it is demonstrated that the composite electrode can be processed for at least 100 full cycles without significant degradation.

Many other applications could profit from the “nanoproperties”. Catalysis has been the traditional area of nanoparticles since decades, but the availability of advanced technologies for the synthesis and characterization of nanostructured materials will support an even increased use in numerous areas of application. Main fields of interest cover energy harvesting, energy conversion and energy storage. It is expected that nanomaterials will increasingly dominate batteries, super caps, fuel cells, or heterojunction solar cells and in most cases, gas-phase synthesis is the method of choice with respect to production rate, purity and costs.

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