Microwave plasma synthesis of Si/Ge and Si/WSi$_2$ nanoparticles for thermoelectric applications

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Abstract
The utilization of microwave-based plasma systems enables a contamination-free synthesis of highly specific nanoparticles in the gas phase. A reactor setup allowing stable, long-term operation was developed with the support of computational fluid dynamics. This paper highlights the prospects of gas-phase plasma synthesis to produce specific materials for bulk thermoelectrics. Taking advantage of specific plasma reactor properties such as Coulomb repulsion in combination with gas temperatures considerably higher than 1000 K, spherical and non-aggregated nanoparticles of multiple compositions are accessible. Different strategies towards various nanostructured composites and alloys are discussed. It is shown that, based on doped silicon/germanium alloys and composites, thermoelectric materials with $zT$ values up to almost unity can be synthesized in one step. First experimental results concerning silicon/tungsten silicide thermoelectrics applying the nanoparticle-in-alloy idea are presented indicating that this concept might work. However, it is found that tungsten silicides show a surprising sinter activity more than 1000 K below their melting temperature.

Keywords: plasma synthesis, nanoparticles, thermoelectrics, computational fluid dynamics

(Some figures may appear in colour only in the online journal)
generator is limited to a fraction of the Carnot efficiency, determined by the dimensionless figure of merit $zT$ defined as

$$zT = \frac{S^2 \sigma}{\kappa_e + \kappa_{\text{lattice}}} \cdot T \quad (1)$$

Where $S$ is the Seebeck coefficient or thermo power, $\sigma$ is the electrical conductivity, while $\kappa_e$ and $\kappa_{\text{lattice}}$ are the electronic and the lattice part of the thermal conductivity, respectively. The numerator $S^2 \sigma$ is called the power factor. By reducing the phonon’s mean free path via introducing grain boundaries, the thermal conductivity can be significantly reduced while the electron transport responsible for the electrical conductivity is much less affected as long as structure dimensions are in the regime of a few ten nanometers. As a result the research with respect to the formation of high-performance thermoelectric materials points towards the introduction of artificial nanostructures to synthesize materials with a significantly lowered thermal conductivity.

Such artificial nanostructures can be based on grain boundaries [6–8], superlattices or perforated structures [9], as well as alloys or segregates of a second phase [10]. Bux et al [8] showed that the thermal conductivity of silicon-based thermoelectrics could be reduced by a factor of more than ten using milling and hot pressing. In a theoretical work, Mingo and Shakouri showed that embedding of silicides consisting of elements with high ordering number into SiGe alloys (nanoparticle-in-alloy approach) can further decrease the thermal conductivity [11].

Bulk thermoelectrics are usually prepared by sintering of nanosized or nanostructured powders. Therefore, the supply of freestanding, suitable nanomaterials is one of the key factors with respect to high-performance thermoelectrics. Along with these requirements, abundance as well as sustainability of the raw material becomes an important criterion for new materials’ developments.

Silicon technology and processing is well established for crystal growth and thin film technology. It is the second most abundant element of the earth crust and available as nanopowder. Hence, the community is ‘desperately seeking silicon’ [12] with specific properties for thermoelectric applications [13].

A versatile tool for the synthesis of soft-agglomerated nanoparticles of all kinds—especially of non-oxidic materials—is the plasma process, as it can provide high reactivity, high temperature, steep temperature gradients and also high purity. This process enables production of all oxidic and non-oxidic materials, for which respective gaseous, liquid, or solid precursors with a reasonable vapor pressure are available. It allows for the synthesis of nanomaterials in a continuous process with kinetic control of the particle formation. Plasma processing can be performed with multiple techniques at very different conditions resulting in thermal plasmas with very high gas temperature in the range of a few thousand Kelvin (usually transferred and non-transferred dc plasma torches and radio-frequency driven high frequency (HF)), very-high frequency (VHF) and ultra-high frequency (UHF) driven plasmas) and non-thermal, intermediate-temperature, and cold plasmas. Plasma synthesis for nanoparticles is a developing technique [14–20], due to the fact that it enables the formation of increasingly interesting, highly specific particles in the 10 nm range. Compared to other gas-phase techniques, plasma synthesis is able to produce comparatively large quantities of non-agglomerated, spherical particles. This is due to the fact that particles suspended in a plasma are highly charged [21], preventing them from agglomeration due to inter-particle Coulomb forces, in addition to temperature effects discussed later.

2. Microwave plasma reactor

According to Jankowski and Reszke [22], a microwave-induced plasma can be generated using the inductive transfer of standing microwaves in a resonant antenna. When utilizing the TM$_{010}$ mode, the maximum field strength is located in the middle of the microwave antenna. The energy transfer of microwave on a charged particle is given by [22]

$$P = \frac{q^2 E_{\text{Max}}^2}{2m} \cdot \frac{\nu_{\text{Koll}}}{\nu_{\text{Koll}} + \omega^2}, \quad (2)$$

with $q$ and $m$ being charge and mass of the particle, $\nu_{\text{Koll}}$ is the collision frequency of the particles, $E_{\text{Max}}$ is the maximum field strength and $\omega$ is the frequency of the microwave [22]. The energy transfer becomes maximum when the excitation frequency matches the collision frequency [23]. Thus, energy transfer in a microwave plasma is based on the energy absorption of the electrons, which are the only particles that can follow the excitation frequency, thus leading to a non-thermal plasma. Palomares et al [24] could show that typical temperatures in microwave-induced plasmas are in the range of 1400 K while the electron temperature was about 10,000 K. This is also in accordance to gas temperature measurements of a microwave-induced plasma using NO-LIF (laser-induced fluorescence of NO molecules) thermometry [25].
Particle formation in a (microwave) plasma is significantly different from particle formation based on the thermal decomposition of a precursor material due to the high number of charge carriers and charging effects. Roth et al. [26] were the first who reported on the formation of silicon particles using RF plasma. In general, the growth of particles from the gas phase can be classified into the initial growth of stable nuclei followed by a rapid growth phase via coagulation and coalescence as well as heterogeneous decomposition of the precursor on the particle surface [27]. Finally, particle growth ends in the growth saturation phase. While the rapid growth phase is dominated by bipolar Coulomb interaction of small, positively charged and fast growing, negatively charged particles [28], mostly positively charged particles are expected in the growth saturation phase of particle formation in a microwave plasma reactor as the ionization of particles by high energy electrons is much more probable than electron capture [23]. The unipolar charging of the particles affects their collision probability $p_{12}$. While the probability for the collision of uncharged particles...
of diameter $d_1$ and $d_2$ is proportional to the square root of their product [23]. $p_{12} \propto \sqrt{d_1 \cdot d_2}$, it is significantly reduced for likely charged particles. The charged particles possess a spherical electrical field constraining further collision [27].

In this case, $p_{12} \propto \sqrt{d_1 \cdot d_2} \cdot (d_1 \cdot d_2)^{-1} = (\sqrt{d_1} \cdot \sqrt{d_2})^{-1}$, which clearly indicates that collision is reduced with increasing particle size. As a result, particle size distribution downstream the particle formation zone of a microwave plasma reactor shows a comparably small particle size distribution as has been shown by means of particle mass spectrometry [29].

The temperature of particles originating from plasma synthesis is usually higher than the surrounding gas temperature due to electron-ion recombination on the particle surface and the impact of ions and electrons. The excess temperature is related to the particle size and can reach a few hundred Kelvin. This heating process leads to an annealing process and is mainly responsible for the fact that particles even from non-thermal plasmas usually exhibit spherical, single crystal-line morphology [28].

This paper will discuss the formation of nanoparticles for thermoelectrics via microwave plasma synthesis and some of their thermoelectric properties. This includes silicon as well as Si/Ge and tungsten silicide as an example for the nanoparticle-in-alloy approach suggested by Mingo et al [11]. Moreover, a modified nozzle design for the injection of the precursor gases is presented which was developed based on 3D fluid dynamics calculations.

4. Reactor setup

The experimental setup used for nanoparticle formation in our lab is based on a commercially available Cyrannus plasma source produced by iplas company (Germany), allowing for the formation of a spherical plasma with a few ten millimeter in diameter. It is connected to a 6 kW microwave generator and was operated as described before [25]. A sketch of the reactor is shown in figure 1. It is oriented vertically and consists of a quartz glass tube with a diameter of 70 mm. The precursor (e.g. monosilane) is injected together with a carrier gas (argon) through a tube with an inner diameter of 6 mm and a length of 30 mm located at the bottom of the quartz tube.

Due to flow instabilities and large recirculation zones, deposition of nanoparticles on the reactor walls and on the nozzle occurs during long-term production (after a few hours of operation). We identified that the coaxial co-flow surrounding the injection nozzle could not feature the desired direction of the carrier gas jet and the wall shielding from the particles. Hence, the inlet of the co-flow was re-designed to meet these requirements by introducing a circumferential velocity field component driving the lower density gases toward the axis of the reactor.

The flow field within the quartz glass tube was calculated by means of a computational fluid dynamics (CFD) in a 3D integration domain. The simulation domain had a length of 250 mm with the center of the spherical microwave plasma located 95 mm above the inlet of the precursor. The new co-flow nozzle is located at the reactor bottom around the precursor inlet pipe as highlighted in yellow in figure 1. For the simulation, a volumetric heat source was used to model the plasma zone. Its shape was received from visual examination and the heat release was adjusted to NO-LIF temperature measurements [25].

To stabilize the injection of the precursor gases, the co-flow nozzle spins the incoming sheath gas, and the evolving swirl flow directs the precursor jet and stabilizes the plasma by keeping the precursor jet centered and avoiding local flapping. Additionally, the sheath gas must shield the reactor wall from particle deposition to keep the windows (for optical access) clean and prevent a pollution of the reactor. The swirl nozzle is intended to lead to a homogeneous, rotational symmetric flow and the carrier gas/precursor jet should have a velocity as high as possible to penetrate the high viscous plasma zone.

Seven designs for injecting the co-flow were tested for their performance: two different types of guide vanes, one with curved (V01) and one with straight vanes (V02), and
a cylindrical domain with the same diameter as the reactor quartz tube with four (T04), 8 (T08) and 12 (T12) tangential holes equally distributed over the circumference. Additionally, two cases were designed where the holes were tilted by 45° in axial direction (T04_45 and T08_45).

3D drawings of the nozzles V01, V02, T04, T04_45 are shown in figure 2 where the inlet for the sheath gas is highlighted in red, the precursor inlet nozzle in green and the blades in blue. Each component domain was added to the reactor domain (the quartz glass tube with a volumetric heat source representing the plasma). The conditions for which the nozzles were tested were the common experimental conditions of the plasma reactor, a pressure of 30 mbar, a carrier gas flow of 3.5 slm Ar, and a sheath gas flow of 10 slm Ar, both with an inlet temperature of 300 K.

To assess the effect of the coaxial co-flow on the stability of the flow field, the circumferential velocity within the quartz tube was analyzed. For most stable conditions it should be high at the reactor walls and low near the centerline of the reactor. This leads to a shielding of the walls and ensures that the precursor/carrier gas jet is directed and not disturbed by the sheath gas.

The circumferential velocity for the seven nozzle designs is illustrated in figure 3 for one time step of the transient simulation. It is obvious that the two designs generating the best swirl flow with respect to the criteria mentioned above are variant T04 and T08. The four tangential holes (T04) lead to a distinct spin with high circumferential velocity near the reactor walls, while the modified tangential holes (rotated 45° in axial direction, T04_45) provide a spin further downstream with much less circumferential velocity. The flow field for the 8 tangential holes also features a high circumferential velocity at the walls, and hence a well-swirled co-flow gas. For these two nozzle types, the distribution of the precursor carrier gas was investigated with respect to the flow of the carrier gas/precursor jet. It has to penetrate the high viscous plasma and should be kept away from the reactor walls by the co-flow. Hence, the mass concentration of argon should be high (~1) near the centerline of the reactor and low (~0) at the wall of the quartz glass tube.

The argon mass fraction for T04 and T08 is shown in figure 4 for one time step of the transient simulation. Due to the higher circumferential velocity of design T04 the carrier gas jet gets more spread. However, design T08 leads to a better shielding of the walls from the carrier gas and therefore was chosen to be the best design variant.

| Table 1. Measured and calculated lattice constants and literature data of Si, Ge and the SiGe alloys produced. |
|---------------------------------------------------------------|
| Nominal composition | Ge | Si_{80}Ge_{20} | Si_{95}Ge_{5} | Si |
| Lattice constant from XRD/nm | 0.5660 | 0.5467 | 0.5445 | 0.5435 |
| Lattice constant calculated/nm | 0.56579 [35] | 0.5476 (calculated according to [35]) | 0.5442 (calculated according to [35]) | 0.5431 [36] |

Figure 7. Si_{80}Ge_{20} nanoparticles from microwave plasma synthesis. Left: bright field TEM image, right: scanning transmission electron microscopy (STEM) image.

Figure 8. Schematic drawing of the reactor setup consisting of two microwave plasma reactors operated in parallel.
A nozzle according to design T08 was constructed and assembled into the reactor, see figure 5. Even for different operating conditions such as higher pressure and modified gas flows it provides stable conditions and less particle deposits at the walls and the optical windows of the reactor. It has been shown that this flow is very stable and allows for the measurement of silicon nanoparticle size distribution downstream the plasma zone by time-resolved in situ laser-induced incandescence measurements (LII) [30].

4.1. Si/Ge nanoparticles

It is known that compared to the pure materials silicon and germanium the thermal conductivity of silicon/germanium alloys is significantly reduced due to fluctuation of the atomic mass [6, 7, 31]. This disturbs the harmonic propagation of phonons in the alloy and is known since more than 50 years [31]. The formation of SiGe alloy nanoparticles from silicon tetrachloride and germanium tetrachloride in a non-thermal RF plasma reactor has been reported by Yasar-Inceoglu et al [32]. They could control the composition of the alloy by adjusting the respective mass flow of the precursor gases and obtained nanoparticles with high crystallinity. Pi and Kortshagen [33] used a similar setup but silane and germane instead of the chlorides. They also obtained the respective alloys; however, they observed a preferential accumulation of silicon within the alloys while part of germanium was deposited at the reactor walls.

Using the experimental setup described above, we have synthesized phosphorous-doped Si/Ge nanoparticles for thermoelectric applications by two different methods. Firstly, two materials were synthesized analogous to Pi and Kortshagen [33] using a mixture of germane and silane plus phosphine as a dopant. The first contains 79.2% Si, 20% Ge, and 0.8% P (Si₈₀Ge₂₀), the second one 94.05% Si, 5% Ge and 0.95% P (Si₉₅Ge₅). The x-ray diffraction analysis (Cu kα) of the alloy material is shown in comparison to pure silicon and germanium nanoparticles (figure 6). As expected, the lattice constant \( a \) and therefore the reflex positions in the diffraction pattern of Si₈₀Ge₂₀ shifts according to Vegard’s law [34]. As reported by Adachi [35], the lattice constant of SiₓGe₁₋ₓ alloys can be calculated as follows: \( a(x) = \)
5.6579 − 0.2269x. The calculated as well as the measured values for the two different samples, Si80Ge20 and Si95Ge5, are summarized in table 1.

The results show a reasonable accordance between expected and measured lattice constants and supports the expectation that the synthesized materials contain the two elements in the ratio that was adjusted by the mass flows.

Transmission electron microscopy (TEM) images of the materials show soft agglomerates of almost perfectly spherical nanoparticles with a mean diameter of a few ten nanometer and a small particle size distribution (figure 7). As described before, this morphology is expected and known for nanoparticles from microwave plasma synthesis. The images give no indication for segregation or formation of a Si/Ge composite as each single particle shows a homogeneous contrast. The energy-dispersive x-ray spectroscopy (EDX) of the sample Si80Ge20 (not shown) yields a Si/Ge ratio of 78/22, which is also in very good agreement with the expectations.

In a second approach, two silicon/germanium composite materials were synthesized by mixing the off-gas of two separate microwave plasma reactors operated in parallel as shown in figure 8.

The x-ray diffraction pattern of the first sample prepared by this method clearly shows the existence of the two separate phases, silicon and germanium (figure 9). The different broadening of the reflexes indicates that the germanium nanoparticles are bigger than the silicon nanoparticles, which could be verified with Rietveld refinement of the pattern using the program MAUD [37]. A mean crystallite size of 22 and 34 nm was calculated for silicon and germanium, respectively. We attribute this difference in particle size to the lower melting temperature of germanium compared to silicon, thus enabling a longer growth period. Based on the x-ray analysis it was found that the two materials synthesized by this method contain 9 (Si91Ge9) and 40% (Si60Ge40) of germanium, respectively.

In comparison to the TEM investigations mentioned before, the image shown in figure 10 clearly indicates that the material consists of two different products, i.e. smaller particles with low contrast and bigger particles with a more pronounced contrast. The same is observed in scanning transmission electron microscopy (STEM) mode, and the EDX analysis of the two areas marked in red supports the assumption that the bright particles consist of germanium while the smaller particles with low contrast are silicon.

Figure 11. Thermoelectric properties of the different silicon/germanium samples. The materials prepared from the alloyed nanoparticles are marked in black and red while the samples prepared from the composites are marked in green and blue. A phosphorous-doped silicon sample (purple line) is shown for comparison.
5. Thermoelectric properties

Bulk thermoelectric materials were prepared from the four nanoparticulate materials using current-assisted sintering at 1050°C, details can be found elsewhere [25]. The Seebeck coefficient $S$ and the electrical conductivity $\sigma$ were measured by a direct measuring technique using the commercial system ZEM-3 from *Ulvac technologies, Inc.* The charge carrier concentration and mobility were determined from a Hall measurement using the van-der-Pauw method for sample structures with arbitrary shape [38]. A laser flash method LFA 457 MicroFlash from *NETZSCH Gerätebau GmbH* was used for the characterization of the thermal transport properties of the sintered samples while the heat capacity was measured using differential scanning calorimetry with an STA449F1 from *NETZSCH*.

Figure 11 summarizes the transport data of the different silicon/germanium samples in comparison to silicon doped with 1% of phosphorous. The Seebeck measurements do not show a clear tendency but it is observed that the germanium-rich samples show the highest Seebeck coefficient. We attribute this to the fact that these materials contain the lowest dopant concentration of 0.8 and 0.6%, respectively. A similar behavior is observed with respect to the electrical conductivity. Here, the samples with the highest germanium content show the lowest values due to reduced charge carrier concentration. Additionally, the high germanium content lowers the charge carrier mobility [39]. Both effects lead to reduced electrical conductivity. The other samples behave similar, as also observed with respect to the Seebeck coefficient.

The thermal conductivity of nanocrystalline thermoelectric materials is significantly decreased compared to the respective bulk materials. Silicon-based thermoelectric materials that were prepared identically to the materials discussed here typically show a mean crystallite diameter of about 110 nm after sintering with a broad size distribution ranging from 50 to 250 nm as received from TEM [40]. Similar values were also observed for SiGe samples shown here. As expected from experimental data as well as from molecular dynamics calculations [41], the thermal conductivity of all germanium-containing samples is significantly reduced compared to that of nanocrystalline silicon ($15 \text{Wm}^{-1} \text{K}^{-1}$) and also in comparison to bulk SiGe alloys. A room temperature value of around $1.5 \text{Wm}^{-1} \text{K}^{-1}$ was measured for Si$_{80}$Ge$_{20}$ which is lower than expected from the calculations of Melis and Colombo [41], who stated that thermal conductivities around $1.5 \text{Wm}^{-1} \text{K}^{-1}$ would require a grain size of about 10 nm. We attribute this discrepancy to a strained lattice [40], which results in a lower value of the thermal conductivity. Consequently, the figure of merit for all germanium-containing samples is substantially increased compared to silicon reaching a maximum value of almost 0.85 for the sample Si$_{91}$Ge$_9$. These results impressively show that nanostructuring of materials via a gas-phase process in combination with alloying can lead to a substantial increase in thermoelectric performance.

5.1. Si/Silicide nanoparticles

In a further set of experiments, the nanoparticle-in-alloy approach suggested by Mingo and Shakouri was investigated.
using the example of tungsten and phosphorous-doped silicon (2% P). Respective materials were synthesized from a homogeneous mixture of monosilane, phosphine and tungsten hexafluoride (WF₆) as gaseous precursor. Composites containing 0.5, 1, and 5 at% of tungsten were prepared with the setup consisting of one reactor. The x-ray investigation of the as-prepared powders clearly showed the expected diffraction pattern of silicon and some additional reflexes that could be attributed to tungsten disilicide (WSi₂), see figure 12. The respective Rietveld refinement using MAUD yielded a mean crystallite diameter of about 5 nm for WSi₂. After sintering, the signals originating from tungsten silicide became much sharper indicating a strong growth of the silicide crystals. However, silicon is still present (reflexes are marked).

To investigate the morphology and the local distribution of silicon and tungsten silicide nanoparticles, the as-prepared samples were dispersed in ethanol, dip-coated on a TEM grid, dried, and investigated with transmission electron microscopy (TEM, Tecnai F20, FEI Company). Due to the high atomic number of tungsten, the tungsten silicide nanoparticles appear as small dark spots while the bigger silicon nanoparticles are much brighter (see figure 13). Both kinds of particles are almost spherical and the image shows a homogeneous intermixture of the two materials. Thus, the TEM results confirm the conclusions of the XRD-measurements.

It can be concluded that our approach towards the synthesis of tungsten silicide nanoparticles alloyed with silicon was successful, however, the established sintering procedure at 1050 °C led to a strong crystal growth of the silicide despite its high melting temperature of 2160 °C [42].

The thermoelectric properties of the sintered bulk materials are summarized in figure 14. It is obvious that the addition of 0.5 and 1 at% of tungsten has only a marginal effect on the transport properties, which is in contrast to the calculations of Mingo et al [11], who predicted a strong effect even for low contents of silicides (less than 1%). This might be due to the fact that we observed a strong sintering leading to large silicide crystals, thus reducing the number concentration of silicide particles that contribute to phonon scattering. The thermoelectric properties change with higher silicide mass fraction. The sample containing 5 at% of tungsten showed a clear increase in Seebeck coefficient and a significantly reduced thermal conductivity compared to silicon and materials with 0.5 and 1% of tungsten. However, it also strongly affects the
electrical conductivity. Nevertheless, the $\varepsilon T$ of this sample is slightly increased compared to the other materials. Materials with higher tungsten silicide content were also investigated; however, they mostly show metallic-like behavior with low Seebeck-coefficients, most probably due to the fact that the percolation threshold is exceeded.

6. Summary

It has been shown that microwave plasma synthesis is a versatile tool to produce nanomaterials with distinct properties. Due to its specific characteristics of enabling temperatures in the range between a few hundred and a few thousand centigrades together with Coulomb repulsion of charged particles, spherical, non-aggregated nanoparticles can be produced featuring small particle size distributions. By means of CFD calculations, stable fluiddynamic conditions allowing for long-term synthesis were examined. Using the example of thermoelectrics, the application of different synthesis strategies such as formation of composites and alloys demonstrate the enormous flexibility of microwave plasma synthesis as an all-in-one device suitable for many purposes with respect to nanoparticle synthesis.

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