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Germanium-silicon alloy and core-shell nanocrystals by gas phase synthesis†

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In this work we present a novel route to synthesize well defined germanium-silicon alloy ($\text{Ge}_x\text{Si}_{1-x}$) and core-shell nanocrystals (NCs) employing monosilane (SiH_4) and monogermane (GeH_4) as precursors in a continuously operated two-stage hot-wall aerosol reactor setup. The first hot-wall reactor stage (HWR I) is used to produce silicon (Si) seed particles from SiH_4 pyrolysis in Argon (Ar). The resulting seeding aerosol is fed into the second reactor stage (HWR II) and a mixture of SiH_4 and GeH_4 is added. The ratio of the precursors in the feed, their partial pressures, the synthesis temperature in HWR II and the overall pressure are varied depending on the desired morphology and composition. Alloy particle production is achieved in the heterogeneous surface reaction regime, meaning that germanium (Ge) and Si are deposited on the seed surface simultaneously. The NCs can be synthesized with any desired composition, whilst maintaining a mean diameter around 30 nm with a geometric standard deviation (GSD) around 1.25. The absorption behavior and the related fundamental optical band gap energy in dependence on the alloy composition are exemplarily presented. They prove the possibility to tailor NC properties for electronical and opto-electronical applications. In the homogeneous gas phase reaction regime faceted Ge-Si core-shell structures are accessible. The Ge deposition on the seeds precedes the Si deposition due to different gas phase reaction kinetics of the precursors. The Si layer grows epitaxially on the Ge core and is around 5 nm thick.

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Introduction

Semiconducting nanocrystals provide various opportunities to tailor their opto-electronic properties *e.g.* for electronic, photonic and energy related applications.¹ One possibility is the reduction of the NC size to affect their bandgap utilizing the quantum confinement effect.² This NC size control is well established for colloiddally synthesized systems like CdSe .³ For some systems the relation between bandgap and NC size is so well-defined, that it is possible to determine the size of particles by analyzing only their optical properties.⁴ Another degree of freedom in engineering NC properties is to introduce compositional variations. Ternary or even quaternary systems like $\text{Cd}_x\text{Zn}_{1-x}\text{Se}$, $\text{CdS}_x\text{Se}_{1-x}$, $\text{HgSe}_x\text{S}_{1-x}$, $\text{CdS}_x\text{Te}_{1-x}$ and $\text{Cu}_2\text{ZnSnS}_4$ are examples for influencing electronic properties

by deliberate incorporation of isovalent elements.^{2,5} However, the broadest scope of technologies has been developed for the group IV semiconductor silicon. Alloying Si NCs with germanium will allow new applications in printed electronics, optoelectronics and photovoltaics.^{6,7} Especially stable dispersions of NCs are possible starting materials in new roll-to-roll low cost fabrication techniques.^{3,8} A very promising field of application are thermoelectric generators, that attracted a lot of attention in the last years. The dimensionless figure of merit $ZT = (S^2\sigma/k)T$ could continuously be increased up to 1.84, reported in 2014 by Basu *et al.*⁹ for a $\text{Ge}_{80}\text{Si}_{20}$ alloy. Z is the thermoelectric figure of merit, S the Seebeck coefficient, σ the electrical conductivity and T the absolute temperature. This composition, around the minimum in the thermal conductivity k , is optimal for maximizing the figure of merit. Furthermore, a nanoparticulate approach can enhance $S^2\sigma$ and also decrease k .⁹⁻¹¹ The synthesis routines for $\text{Ge}_x\text{Si}_{1-x}$ particles and layers are manifold. One example for a liquid phase process is described by Barry *et al.*² who use hydrogen silsesquioxane and soluble germanium diiodide complexes to synthesize $\text{Si}_x\text{Ge}_{1-x}$ NCs. Mechanical alloying by ball milling of Si and Ge chunks is for example reported by Wang *et al.*¹¹ Gas phase processes are mostly used to produce either nanowires or planar films. The synthesis techniques include (low

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pressure) chemical vapor deposition (CVD) with subsequent annealing,^{12,13} laser crystallization,¹⁴ Ge⁺ implantation,^{15–17} and microwave processing.^{7,18} A recent review on synthesis routes for 1D semiconductors is given by Barth *et al.*¹ Most suitable for the synthesis of freestanding NCs with reasonable production rate and continuous as well as scalable process design, however, are aerosol synthesis techniques.¹⁹ Very convincing results are achieved with non-thermal plasma reactors utilizing the gaseous precursors SiH₄ and GeH₄⁶ or more recently silicon and germanium tetrachloride,⁸ resulting in particles smaller than 10 nm. Erogbogbo *et al.* apply laser induced simultaneous pyrolysis of SiH₄ and GeH₄ in an aerosol reactor. The resulting nanocrystals are dispersed in suitable solvents and can then be used as ink for thin film formation.³ Particle synthesis in hot-wall reactors is a simple, versatile, cheap and scalable technique. The results presented here are based on our previous works. We have shown that hot-wall reactors can be used to obtain quite narrow particle size distributions of Si NCs. The NC size and the width of the size distribution can be tailored by rigorous mathematical optimization.²⁰ Further, we have shown ways towards shape control²¹ and demonstrated how to produce patchy and Janus-like particles.²² Utilizing a two-stage hot-wall reactor setup with SiH₄ and GeH₄ as precursors this work presents a simple, continuous and scalable process for Ge–Si alloy NC synthesis. The first hot wall reactor stage (HWR I) is exclusively used to produce a seeding aerosol stream at constant volume flow rates. In the second stage (HWR II) SiH₄ and GeH₄ are added. This so called seeded synthesis²³ positively influences the product morphology. The mixing of the two precursors complicates the gas phase chemistry for both components and may lead to particle populations of different composition within the final product.^{3,24} We demonstrate, that by combining seeding (in a first reactor) and mixing of the precursors (in a

second reactor) the complexity of the system can be exploited to synthesize, in a controlled way, either Ge–Si alloy NCs of any desired composition or generate well-defined Ge–Si core–shell particles.

Results and discussion

*Seeding*²³ is performed to synthesize all the various samples in this study. It is beneficial in order to produce homogeneous products exhibiting well-defined properties like a reproducible narrow size distribution. To this end constant SiH₄ and Ar volume flow rates are fed into HWR I at the conditions specified for each sample (see Materials and methods section). For more details about the seeding please refer to the ESI.†

Growth mode diagram

GeH₄ and SiH₄ are fed into HWR II at 800 °C growth temperature. The so called nominal Ge content x_{Ge}^0 is determined by the molar feed ratio of GeH₄ to SiH₄. For all samples shown in Fig. 1 the molar feed ratio is unity and x_{Ge}^0 equals 0.5. The resulting nominal alloy composition is Ge_{0.5}Si_{0.5}. The Ge content measured by various techniques is called actual Ge content x_{Ge} and can significantly differ from the nominal Ge content. The total system pressure P_{tot} is varied between 25 and 150 mbar in steps of 25 mbar. Experiments are conducted at a fixed sum of the GeH₄ and SiH₄ partial pressures ($\sum p_{\text{Prec}}$) and their volume flow rates are adjusted accordingly. Samples of the resulting NCs are prepared using a low pressure impactor (see Materials and methods section). Fig. 1 summarizes the experiments conducted in this manner. All NC samples are analyzed by scanning electron microscopy (SEM) and Raman spectroscopy. The results of representative high-angle annular dark-field scanning transmission electron microscopy (HAADF

Fig. 1 Experimental and schematic growth mode diagram of a seeded mixture of SiH₄ and GeH₄ with fixed $\sum p_{\text{Prec}}$ at given system pressure P_{tot} and 800 °C growth temperature in HWR II. Nominal composition is Ge_{0.5}Si_{0.5}. Samples investigated in more detail in the following are marked with consecutive numbers (1–8). Zones of differing morphology are discriminated by their symbols. Zone 1: heterogeneous surface reaction regime (spheres). Zone 2: homogeneous gas phase reaction regime (filled hexagons). Zone 3: additional homogeneous nucleation occurs, leading to a second particle species in the samples (dots in hexagons).

STEM) investigations support the interpretation of the experimental findings. These investigations divide the diagram in Fig. 1 in three distinct zones and a transition zone concerning morphology and composition. This behavior is explained with different growth modes in the following, making Fig. 1 an growth mode diagram of a seeded mixture of SiH_4 and GeH_4 (equimolar) at 800 °C growth temperature. Conducting the same experiments at elevated temperature will shift the transition zone towards higher total and partial pressures, enlarging zone 1. This will not be shown, because it is accompanied by a degradation of the morphology of zone 2 particles.

The morphology of exemplary samples from different zones is shown in the ESI (ESI Fig. 3†). Sample 1, chosen as an example for zone 1 alloy nanoparticles, shows spherical non-sintered particles of a very uniform shape and size of 21.5 nm with a geometric standard deviation of 1.14 ($\text{GSD} = 1.14$). The particles in zone 2 (sample 7) are all faceted and isolated polyhedrons (*cf.* also Fig. 6). Very few hard aggregates are observed. Between the two zones lies a transition zone where the resulting particles show first facets. Many structures are hard aggregates of primary particles. In zone 3 the particle ensemble becomes very broadly distributed concerning size and shape. Spherical particles are formed in addition to the faceted polyhedrons. They are considerably smaller than the faceted structures and are the result of homogeneous nucleation. Defined product morphology, however, is only achieved in zones 1 and 2, which are therefore investigated in more detail.

Raman analysis in order to determine the actual Ge content x_{Ge} of the produced particles and the degree of the intermixing between Si and Ge Raman analysis was applied. By determining the position of the strong first order lines resulting from the nearest neighbor atomic vibrations of Ge-Ge, Ge-Si and Si-Si Raman analysis allows for the determination of x_{Ge} (see Materials and methods section) according to Reparaz *et al.*,²⁵ Tsang *et al.*²⁶ and Alonso and Winer.²⁷ In Fig. 2 the positions of these peaks are shown for seven representative samples from zone 1 (samples 1 to 3), the transition zone (sample 4) and zone 2 (samples 4 to 7). For visualization the spectra of samples 1 and 7 are plotted normalized between 0 and 1 with respect to the Ge-Ge peak. The inset shows the magnified region of the Si-Si peak. For representative Raman spectra of all seven samples please see ESI Fig. 4.† The dependency of the peak positions on the precursor partial pressures and the total pressure is directly connected to the observed morphological changes. In the following completely strain free particles are assumed. Sample 1 shows a Ge-Ge peak at $294.0 \pm 0.8 \text{ cm}^{-1}$. According to eqn (2) (see Materials and methods section) this corresponds to an actual composition of $\text{Ge}_x\text{Si}_{1-x}$ with $x_{\text{Ge}} = 0.73 \pm 0.04$ respectively. Energy-dispersive X-ray spectroscopy in the SEM (EDXS) analysis yields $x_{\text{Ge}} = 0.73 \pm 0.01$, which is in excellent agreement.

Please note, that the stated errors are a standard deviation between all measurements performed on a sample. The systematic error from the Raman equipment is 0.02, for EDXS no systematic error can be specified (see Materials and methods section for more details). The fact that the actual Ge content

Fig. 2 Evolution of the Raman peaks of seven representative samples from zone 1 and 2 as well as the transition zone. As an example the normalized spectra of samples 1 and 7 are shown on the right. The inset shows a magnification of the Si-Si peaks at their actual position. Sample 2: $\sum p_{\text{Prec}} = 1.55 \text{ mbar}$, $P_{\text{tot}} = 25 \text{ mbar}$; sample 3: $\sum p_{\text{Prec}} = 1.07 \text{ mbar}$, $P_{\text{tot}} = 50 \text{ mbar}$; sample 4: $\sum p_{\text{Prec}} = 1.61 \text{ mbar}$, $P_{\text{tot}} = 50 \text{ mbar}$; sample 5: $\sum p_{\text{Prec}} = 2.58 \text{ mbar}$, $P_{\text{tot}} = 75 \text{ mbar}$; sample 6: $\sum p_{\text{Prec}} = 3.14 \text{ mbar}$, $P_{\text{tot}} = 75 \text{ mbar}$.

differs significantly from the nominal Ge content of $x_{\text{Ge}}^0 = 0.5$ will be discussed separately in the section about Ge-Si alloy NC synthesis in zone 1. Sample 7 does not show the typical spectrum expected for a homogeneous alloy. The Si-Si peak is centered at $508.2 \pm 1.6 \text{ cm}^{-1}$ and the Ge-Ge peak at $299.5 \pm 0.3 \text{ cm}^{-1}$. This corresponds to two broadly differing Ge contents of $x_{\text{Ge}} = 0.18 \pm 0.02$ (Si-Si peak evaluation, eqn (1)) and $x_{\text{Ge}} = 0.95 \pm 0.01$ (Ge-Ge peak evaluation, eqn (2)), respectively. The Si-Si peak in all spectra of zone 2 (and zone 3, not shown) samples is distinct and indicative of a Si-rich region in the samples. These results show, that in zone 2 a separation between Si and Ge occurs. Areal analysis by EDXS yields $x_{\text{Ge}} = 0.65 \pm 0.01$ and is understood as mean composition of the whole sample. The morphological change occurring between zones 1 and 2 is thus accompanied by a separation of Si and Ge in zone 2, while in zone 1 homogenous Ge-Si alloy NPs can be produced. In the transition zone the spectra show a wide variation of peak positions as indicated by the high standard deviation. In this zone alloy as well as Ge- and Si-rich particles form. A separation of Si and Ge in the observed manner cannot be explained by a miscibility gap. Ge and Si exhibit full miscibility over the whole compositional range.^{28,29} The drastic differences in particle morphology and composition that have been revealed between the zones in Fig. 1 can, however, be explained by different growth modes in the respective regimes/zones. The explanation follows the idea of a kinetic model for Ge-Si alloy growth by CVD from gaseous precursors.^{24,30} It distinguishes between the heterogeneous decomposition of adsorbed precursor molecules on a surface (*i.e.* the Si nuclei of the seeding aerosol from HWR I) and the homogeneous decomposition of the precursor molecules in the gas phase. This is illustrated in Fig. 1 and will be discussed for zones 1 and 2 in the following.

Ge-Si alloy NC synthesis in zone 1 is investigated in more detail by keeping $\sum p_{\text{Prec}}$ and P_{tot} constant (0.34 and 25 mbar,

Fig. 3 (a) Actual Ge content x_{Ge} measured by EDXS dependent on the synthesis temperature T in HWR II. Nominal Ge (feed) content $x_{\text{Ge}}^0 = 0.5$. $\Sigma p_{\text{Prec}} = 0.34$ mbar; $P_{\text{tot}} = 25$ mbar. (b) Representative Raman spectra of samples with nominal Ge content of $x_{\text{Ge}}^0 = 0.1$, $x_{\text{Ge}}^0 = 0.5$ and $x_{\text{Ge}}^0 = 0.8$ synthesized at 1000 °C synthesis temperature in HWR II. (c) Actual Ge content x_{Ge} measured by EDXS and Raman plotted against the nominal Ge content x_{Ge}^0 derived from the $\text{GeH}_4/\text{SiH}_4$ feed ratio. The deviation ranges between 1 to 9 at%, depending on the sample and the measurement technique. A Ge enrichment is observed in every sample (see: discussion of the particle formation mechanism in zone 1 and ESI†).

sample 1 conditions) and performing a synthesis temperature variation in HWR II as well as a variation of the $\text{GeH}_4/\text{SiH}_4$ feed ratio. Fig. 3a shows five samples synthesized with a nominal Ge content of $x_{\text{Ge}}^0 = 0.5$ at different temperatures in HWR II. Their actual Ge content x_{Ge} is measured by EDXS (SEM). It becomes clear, that with increasing synthesis temperature the Si content in the samples increases and the actual Ge content comes close to the nominal Ge content. The difference in x_{Ge} between 1000 °C ($x_{\text{Ge}} = 0.56 \pm 0.01$) and 1100 °C ($x_{\text{Ge}} = 0.55 \pm 0.01$) synthesis temperature in HWR II is negligible. Consequently, to lower the thermal load of the reactor system and reduce possible sintering effects, the alloy NCs are synthesized at 1000 °C. Nominal Ge contents ranging from $x_{\text{Ge}}^0 = 0.1$ to $x_{\text{Ge}}^0 = 0.9$ are set in intervals of 10 at%. The actual Ge content x_{Ge} is determined by EDXS and Raman spectroscopy. For the Raman analysis completely strain free particles are assumed. Fig. 3b shows representative Raman spectra of samples with different nominal Ge contents.

The evolution of the peak positions corresponds to a change in composition of a pure alloy.^{6,8,31} Actual compositions of $x_{\text{Ge}} = 0.09 \pm 0.01$, $x_{\text{Ge}} = 0.54 \pm 0.01$ and $x_{\text{Ge}} = 0.82 \pm 0.01$ are derived from the three exemplary spectra, which are in excellent agreement with the nominal compositions. For details about the determination of the composition *via* Raman spectroscopy, please see the Materials and methods section. Exemplary Raman spectra of all samples can be found in the ESI (cf. ESI Fig. 4†). Complementing the Raman results by areal EDXS leads to the plot in Fig. 3c, which shows the deviation of the actual from the nominal Ge content. It becomes clear that at 1000 °C in HWR II Ge–Si alloy particles in the whole compositional range can be synthesized by varying the ratio of the precursors GeH_4 and SiH_4 in the feed of HWR II. Additionally, powder samples (see Materials and methods section) of selected nominal Ge contents are prepared at the same process conditions and analyzed by conventional bright-field TEM (BFTEM), selected-area electron diffraction (SAED) and high-resolution TEM (HRTEM). Representative particles of the respective powders are shown at low and high magnification in Fig. 4. Independent of the composition of the alloy

the particles are perfectly spherical, monocrystalline and free of extended defects. Moreover, PSDs for the different products were derived from those images (cf. ESI Fig. 9†). The diamond structure of the Ge–Si alloy is verified by electron diffraction as the insets in Fig. 4 demonstrate. However, the quantitative evaluation of the electron diffraction patterns regarding particle size and alloy composition was discarded in favor of quantitative X-ray diffraction (XRD) analysis. It allows for probing much larger numbers of particles and is thus more representative. As complementary technique for composition determination of Ge–Si alloys, it is used to validate the EDXS and Raman results in the ESI (cf. ESI Fig. 5 and 6†).

To prove, that fundamental properties of the material are altered depending on the composition diffuse reflectance ultraviolet-visible light (DR-UV/VIS) spectroscopy is performed. In Fig. 5a five alloys and pure Si and Ge powder absorption spectra are depicted. The onset of absorption clearly is shifting towards higher wave lengths with rising Ge content, proving the decreasing fundamental energy gap. Fig. 5b summarizes the energy gaps connected to the absorption onsets in relation to literature values. It is obvious, that our alloy NCs follow the trends. In the region of the Si like delta conduction band minimum (Si rich alloy powders) the energy gap very closely resembles the analytical expression utilized by Krishnamurthy *et al.* to determine alloy-scattering-limited electron mobility in semiconductor systems with multiple band minima.³³ In the Ge rich region the transition to the Ge like L conduction band type is also observed in our powder samples. The decrease in the energy gap is more rapid in this region and our powder samples best resemble the results presented by Braunstein *et al.*³⁴ This means, that the powders can be tailored for electronical and opto-electronical applications.

The particle formation mechanism in zone 1 is discussed in the following. Low total pressure and low precursor partial pressures favor the adsorption of the precursors on the Si nuclei from HWR I. This is first of all due to the fact, that SiH_4 as well as GeH_4 decomposition requires Ar for the three-body-collision reaction leading to hydrogen elimination.^{35–37} Thus low total pressure and low precursor partial pressures decrease

Fig. 4 BFTEM and HRTEM images of Ge–Si alloy NC powder samples A–C synthesized at sample 1 conditions with the following nominal Ge contents: powder A: $x_{\text{Ge}}^0 = 0.7$; powder B: $x_{\text{Ge}}^0 = 0.5$; powder C: $x_{\text{Ge}}^0 = 0.3$. The insets in the BFTEM images show SAED patterns of the respective particles.

the decomposition in the gas phase and hence increase the flux of unreacted precursor onto the surface of the Si-seeds. There the reaction rates for heterogeneous surface reaction are determined by the Ge–H and Si–H bond strength. At low temperatures Si–H decomposition is much slower than Ge–H decomposition,³⁰ which leads to a Ge enrichment in the resulting alloy.³⁸ Increasing temperature leads to increased Si–H decomposition compared to Ge–H decomposition and hence

increasing Si content in the alloy.^{24,39} Consequently, at temperatures high enough for nearly equally fast Ge–H and Si–H decomposition the alloy composition will approach the value adjusted by the precursor ratio. However, a slightly increased Ge content compared to the feed ratio is still observable at feasible synthesis temperatures in HWR II. In this regime no separation between Si and Ge occurs and it is therefore the working regime for alloy NC production with any desired com-

Fig. 5 (a) Absorption spectra of Ge–Si alloy powders with differing Ge content as determined by XRD. The spectra are normalized between 0 and 1 in respect to their highest value and shown between 900 and 1900 nm wavelength of incident light. (b) Fundamental band gap of the powder samples resulting from the onset of absorption. The corresponding Ge content x_{Ge} as determined by XRD and EDX is displayed. This represents the uncertainty in determining the composition. For comparison the fundamental band gap of unstrained Ge–Si alloys according to Weber and Alonso,³² Krishnamurthy *et al.*³³ and Braunstein *et al.*³⁴ are shown.

position at 1000 °C synthesis temperature in HWR II. The compositional control allows for tailored product properties for electronic and opto-electronic applications. We want to especially point out, that also the optimum composition for thermoelectric application is accessible and for a future work both, p- and n-doping of the particles is planned.

Ge–Si core–shell NC synthesis in zone 2 in order to clarify the particle architecture of zone 2 samples which all show a separation between Si and Ge (see Raman results) HAADF-STEM imaging is exemplarily performed on sample 7. Fig. 6a–c shows the resulting micrographs. Due to the larger atomic number Ge appears brighter than Si. It is recognizable that Si forms a well-separated shell around faceted Ge particles. The Si layer is between 5 to 10 nm thick and grows faceted as well. Those particles are very narrowly distributed in size around 89 nm (diameter equivalent sphere) with a GSD of 1.08. Furthermore, the micrographs show some particles containing one or two additional Si-rich inner cores. The fraction of those particles is around 10% in number. The Si-rich inner cores show a mean size of 32 nm with a GSD of 1.12. Particles containing such cores are around 107 nm (diameter equivalent sphere) in size with a GSD of 1.08 (all PSDs determined utilizing STEM images). Si-rich cores are believed to be the result of the seeding process, which is still important for the morphology of the sample (see ESI†). At 75 mbar a fraction of larger Si particles is formed in HWR I (fraction of the seeding aerosol for HWR II). The addition of the volume of a Si inner core and the volume of a particle without results in a diameter of 90.4 nm. The discrepancy between this value and the actual size of 107 nm of the particles containing a Si inner core means that those particles grow faster. This is reasonable when considering that two species of seeds enter HWR II. The higher surface area of the Si particle fraction with 32 nm dia-

meter will lead to a higher flux of precursor molecules onto the surface resulting in a higher growth rate compared to the very small diameter fraction. To investigate the local composition of those particles in more detail, meaning especially to prove the high Si concentration in the inner sections and the outer shell, STEM imaging is complemented by electron diffraction (Fig. 7a) and quantitative EDXS line-scan measurements across those particles (Fig. 6b and c). In contrast to the alloy particles with homogeneous composition (Fig. 4, insets), a systematic peak broadening or even a clear peak splitting of approximately 4% is observed in SAED (Fig. 7a, inset). Considering a similar difference in lattice constants of pure Si and pure Ge, this indicates a distinctive chemical separation within those core–shell particles. As such diffraction analyses do not reveal the local distribution of Si and Ge a site-specific EDXS analysis is conducted. While the EDXS line scan obtained from a particle of the major fraction (without Si inner section) shows a Si signal that almost originates from the Si-rich outer shell (Fig. 6b), the Si-rich inner section of a respective particle is clearly reflected in the line-scan data (Fig. 6c). For more quantitative comparison, the expected elemental distributions obtained from two model particles (*i.e.* spherical particles) one with a 22 nm Si core (corresponding to the measurement), the other without, each with a Si shell thickness of 6 nm (estimated from HRTEM measurements), are plotted in the graphs. These distributions were derived by calculating the local Si and Ge concentrations from weighted projections along the incident beam direction assuming a complete local separation of Si and Ge. It can be seen that the calculated curves within this simple model already describe the measured distributions quite well. Due to the intrinsic absorption of the Si X-rays within the Ge-rich regions of the particles, the local Si signals are expected to be slightly under-

Fig. 6 (a–c) HAADF-STEM micrographs of sample 7. All particles show a Si shell around a faceted Ge structure. (c) An additional Si inner core is found in 10% of the NCs. (b, c) EDXS line-scan measurements performed across two representative particles confirm this arrangement (along arrows). The pictographs show the assumed material distribution of Ge and Si for the spectrum modeling.

estimated in the experimental curve. However, in the region near the Si-rich core (see graph in Fig. 6c) the relatively low Si concentration cannot completely be explained by X-ray absorption. For maximal 50 nm Ge around the Si inner section one only has to expect a reduction of the original Si signal by about 10% (see Materials and methods section). This assumption does not take into account the Si diffusion from the inner section into the Ge which will take place to some extent. This, along with the Raman results of sample 7 which also suggest Ge diffusion into the Si outer layer, might explain the differences.

The Ge diffusion is very slow under strain free conditions^{40,41} and seems to be enhanced by the growth mechanism as discussed in the following. The deposition of Si on Ge is governed by the 4.2% lattice mismatch between the two materials. Thus, a relatively high density of defects like dislocations and stacking faults within the highly crystalline Si layer appear. Furthermore, some of the highly crystalline Ge cores appear to be heavily twinned (Fig. 7a and b). The Si shell grows epitaxially onto the underlying Ge (Fig. 7c and d). In literature the growth mode is described by two mechanisms.

Fig. 7 Conventional bright-field TEM (a, b) and HRTEM (c, d) micrographs of sample 7. The exemplary particle in c and d shows a Si shell around a faceted Ge structure. Both are crystalline and Si grows epitaxially on the Ge core. An amorphous layer of native silicon oxide covers the whole surface due to the sample transfer in air. Complementary to Raman, SAED (exemplary pattern as inset in a) corroborates the chemical separation of Si and Ge within those particles, as the observed rings of reflections broaden (rings of {111}, {022} reflections) or even split up (ring of {113} reflections) according to the lattice mismatch between Si and Ge.

First reports stated the Volmer–Weber growth mechanism for Si on Ge surfaces.⁴² This means that the Si grows as islands without planar film formation at low Si growth rate or coverage. Closed and planar crystalline films finally result from growth on coalesced Si islands.^{43,44} The transition between island and film formation by coalescence is thereby dependent on the Si growth rate or coverage and the growth temperature. More recent publications claim that the Si growth progresses *via* the Stranski–Krastanow⁴⁵ growth mode. The initial planar film growth (wetting layer) is followed by island formation on the wetting layer. Thick planar Si films finally are the result of Ge segregation into the wetting layer which is causing an increased Si deposition rate between the already existing islands. This is due to the increased hydrogen desorption from Ge sites compared to Si sites.^{46,47} Assuming no pronounced strain effects due to the high dislocation density the Raman analysis of sample 7 suggests that the Ge intermixing in the Si wetting layer is happening, which would support Stranski–Krastanow growth. However, the frequency shifts in the Raman could also be caused by strain effects. In

order to clarify the exact mechanism including strain relaxation *via* defect nucleation and interdiffusion in our case, TEM analyses of cross section samples is planned for future works. The faceted form of the final particles is explained by the faceted growth of pure Ge as Cernetti *et al.* showed for nonthermal plasma synthesis of faceted germanium nanocrystals.⁴⁸

The particle formation mechanism in zone 2 is discussed in the following. Increased total pressure and increased precursor partial pressures favor increased homogeneous gas phase reaction rates. However, at 800 °C only the GeH_4 is very reactive^{36,37} and under hydrogen elimination forms germylene (GeH_2), which is the major species in Ge deposition.³⁵ This leads to pure Ge deposition on the seeding aerosol surface as long as GeH_2 is present in the gas phase in HWR II. After it is depleted the SiH_4 can react on the Ge surface heterogeneously to form a Si layer around the Ge. This practically divides HWR II kinetically into a germanium and a silicon deposition step, making zone 2 the working regime for Ge–Si core–shell particle synthesis.

Conclusion

By systematically studying the dependency of Ge–Si NC growth on the total pressure and the partial pressures of the precursors SiH_4 and GeH_4 we derived a comprehensive growth mode diagram for the binary system. It clearly shows two regimes. In the heterogeneous surface reaction regime well-defined strain free Ge–Si alloy nanoparticles with any desired composition are obtained by variation of the precursor feed ratio. The NCs are predominantly of spherical shape and well-separated. The successful tailoring of NC properties needed for application in electronical and opto-electronical devices is demonstrated by the absorption behavior of alloy NC powders with varying composition. Further, we demonstrate Ge–Si core-shell structure synthesis by kinetic decoupling of Ge and Si deposition in HWR II at 800 °C synthesis temperature in the homogeneous gas phase reaction regime. Finally both NC species are thoroughly analyzed regarding their morphology, composition and architecture.

Materials and methods

The reactor setup used in this work is the same as recently described for the synthesis of anisotropic silicon germanium hybrid nanoparticles.²² It basically consists of two consecutive hot wall reactors denoted as HWR I and HWR II. Sampling *via* a low pressure impactor (LPI) creates a small spot of particles on a Si wafer substrate or TEM grid for rapid parameter screening. The sample is sucked from the center of the process tube and represents optimal and homogeneous process conditions. Samples for powder characterization are synthesized using the mini-filter. They generally show a larger GSD and higher mean size in the PSD compared to LPI samples. This is due to a residence time distribution and a radial temperature distribution in the process tube.⁴⁹ Consequently LPI samples are a fraction of the powder samples and properties assigned to powder samples also apply to LPI samples. Powder production rates roughly are 0.5 g h^{−1} for sample 1 condition particles at 1000 °C in HWR II (for $\text{Ge}_{0.5}\text{Si}_{0.5}$ composition) and 1.5 g h^{−1} for sample 7 condition powders (not shown in this work). In this study the first hot wall reactor is exclusively for seeding HWR II by SiH_4 pyrolysis at 900 °C and the given process pressure (depending on the type of product). To this end SiH_4 with a flow rate of 4 cm³ min^{−1} is diluted in 2.4 l min^{−1} argon (normal conditions) and fed into HWR I resulting in the seeding aerosol. In-between HWR I and HWR II GeH_4 , SiH_4 and Ar are added. The sum of the SiH_4 and GeH_4 partial pressures is varied from 0.32 to 6.27 mbar. The $\text{SiH}_4/\text{GeH}_4$ ratio is varied according to the desired product composition. The total pressure ranges from 25 mbar to 150 mbar. The temperature in HWR II is set to either 800 °C or 1000 °C depending on the desired product. In all experiments the volume flow rates of the gases added to HWR II are controlled in such a way, that the partial pressures can be set correctly. This can only be achieved by accepting varying residence times in HWR II.

Sampling for electron microscopy analysis *via* the LPI is directly done onto Si wafer substrates (gold coated for EDXS and Raman measurements) or Lacey Carbon support grids for TEM investigation. For further analysis powder samples are dispersed in ethanol and drop casted onto similar substrates. SEM imaging is performed with a Zeiss Gemini Ultra 55 and particle size analysis conducted with the software ImageJ. For reliable statistics at least 150 particles are evaluated regarding their properties. EDXS is performed in the SEM with an EDXS-detector from Thermo Electron Corporation (Model: NSS 302). The software Noran System Six Version 1.8 from Thermo Electron Corporation is employed to quantify the composition, using implemented theoretical ionization cross sections and the Si–K and the Ge–L emission lines (10 kV accelerating voltage). The quant fit method is “Filter Without Standard” and the matrix correction type is “Proza” (Phi–Ro–Z). The resulting ratio between Ge and Si atomic percentage is used to determine the actual Ge content x_{Ge} of a $\text{Ge}_x\text{Si}_{1-x}$ alloy. Three to five areal measurements are conducted at different positions of one sample, probing at least 9 μm². Full scale counts are never less than 8000 and normally around 15 000. No systematic error of the equipment can be specified. Error bars et cetera correspond to the standard deviation between all measurements performed on one sample. SAED measurements are performed using a Philips CM30 transmission electron microscope. HRTEM, HAADF-STEM and EDXS line scans are performed using an image-side aberration-corrected FEI Titan³ 80–300 transmission electron microscope operated at an acceleration voltage of 200 kV. The EDXS line scans, recorded to determine the local elemental composition of the particles, are obtained in STEM mode using an EDAX Si(Li)-detector. Theoretical ionization cross-sections and fluorescence yields, as implemented in the FEI software, are used to quantify the local composition. Therefore, the Si–K and Ge–Kα emission lines are utilized. Due to the complexity of the particle architecture (Si inner region, Si shell), secondary processes like X-ray absorption and fluorescence, although pronounced for the Si–K emission lines in Ge, have been neglected. Using an X-ray mass attenuation coefficient for Si–K in Ge of 3.6 × 10³ cm² g^{−1} (compared to around 40 cm² g^{−1} for Ge–K in Si, Ref. <http://www.nist.gov/pml/data/xraycoef/>) already leads to absorption of Si–K by around 10% within 50 nm Ge (max. Ge thickness around Si inner regions). Thus, the concentrations presented in Fig. 6 slightly underestimate the local Si content. DR-UV/VIS spectroscopy is performed using a LAMBDA 950 UV/Vis/NIR spectrophotometer from Perkin Elmer, equipped with an integrating sphere. Powder samples are filled into SUPRASIL cuvettes from Hellma Analytics, forming a densely packed and 10 mm thick layer. The reflectance spectra are measured and transformed into absorption spectra by assuming zero transmittance. The absorption spectra show the onset of absorption at a certain wavelength which is indicative of the fundamental band gap of the material. The onset of absorption is determined by the zero of the normalized absorption spectra shown in Fig. 5a and taken as value for the band gap. These values can also be obtained

Fig. 8 Exemplary Raman spectrum with the integral peak centers marked used for composition evaluation.

from Tauc plots.^{50–52} Raman spectra are obtained using a LabRAM HR Evolution analytical Raman microscope from Horiba and 633 nm excitation wavelength of a HeNe-laser. The equipment delivers a 0.3 cm^{-1} resolution of the peak position, resulting in 2 at% measurement uncertainty in the composition. The wavelength is best suited for Ge rich alloys with compositions of $x_{\text{Ge}} > 0.5$.²⁶ Moreover it is possible to avoid altering the sample by e.g. sintering, which would influence the composition as known from literature.⁶ Utmost care is taken in order to prevent sample alteration. For this purpose the laser spot is focused by a $10\times$ -objective resulting in $3.09\text{ }\mu\text{m}$ spot-size. The nominal laser power is 0.0126 W . This means that approximately 200 kW cm^{-2} are dumped into the sample. An acquisition time of 30 s is thus not enough to alter the samples. However, the signal to noise ratio decreases and the spectra do not show high intensities. Evaluation of the spectra is done with the software Origin, as exemplarily shown in Fig. 8.

The peak position ω of either the Si-Si or the Ge-Ge peak is used to evaluate the actual composition x_{Ge} following eqn (1) and (2) respectively.²⁵ The prominent peak of each spectrum is used for this determination, i.e. the Ge-Ge peak for $0.9 \leq x_{\text{Ge}} \leq 0.6$ and Si-Si peak for $0.5 \leq x_{\text{Ge}} \leq 0.1$.²⁶ Three spectra are analyzed in this manner and a mean composition as well as a standard deviation is derived for every sample. The standard deviation lies within the range of the measurement uncertainty for all samples analyzed for their composition.

$$\omega_{\text{Si-Si}} = 520.7 - 68x_{\text{Ge}} \quad (1)$$

$$\omega_{\text{Ge-Ge}} = 284 + 5x_{\text{Ge}} + 12x_{\text{Ge}}^2 \quad (2)$$

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