Pushing the Composition Limit of Anisotropic Ge$_{1-x}$Sn$_x$ Nanostructures and Determination of Their Thermal Stability

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ABSTRACT: Ge$_{1-x}$Sn$_x$ nanorods (NRs) with a nominal Sn content of 28% have been prepared by a modified microwave-based approach at very low temperature (140 °C) with Sn as growth promoter. The observation of a Sn-enriched region at the nucleation site of NRs and the presence of the low-temperature α-Sn phase even at elevated temperatures support a template-assisted formation mechanism. The behavior of two distinct Ge$_{1-x}$Sn$_x$ compositions with a high Sn content of 17% and 28% upon thermal treatment has been studied and reveals segregation events occurring at elevated temperatures, but also demonstrates the temperature window of thermal stability. In situ transmission electron microscopy investigations revealed a diffusion of metallic Sn clusters through the Ge$_{1-x}$Sn$_x$ NRs at temperatures where the material composition changes drastically. These results are important for the explanation of distinct composition changes in Ge$_{1-x}$Sn$_x$ and the observation of solid diffusion combined with dissolution and redeposition of Ge$_{1-x}$Sn$_x$ ($x > y$) exhibiting a reduced Sn content. Absence of metallic Sn results in increased temperature stability by ~70 °C for Ge$_{0.72}$Sn$_{0.28}$ NRs and ~60 °C for Ge$_{0.83}$Sn$_{0.17}$ nanowires (NWs). In addition, a composition-dependent direct bandgap of the Ge$_{1-x}$Sn$_x$ NRs and NWs with different composition is illustrated using Tauc plots.

INTRODUCTION

Group IV semiconductor nanowires are potential building blocks for different fields of application including electronic and optoelectronic devices. However, the performance of Si- and Ge-based materials in optics and photonics is limited by their indirect bandgap. Theoretical and experimental reports describe a modification of the Ge band structure to make direct gap emission more favorable by using tensile or uniaxial strain. Alternatively, the light emission and absorption characteristics of Ge change dramatically, when a threshold concentration exceeds ~8–10% Sn in Ge$_{1-x}$Sn$_x$ rendering it in a direct bandgap material which was experimentally observed and also calculated. Ge$_{1-x}$Sn$_x$ is compatible with CMOS processing based on Si technology and therefore an ideal candidate for infrared optoelectronics and optical devices, such as infrared lasers, photodetectors or light-emitting diodes. In addition, the electronic properties are also altered upon Sn incorporation in the Ge matrix which should result in an enhanced electron and hole mobility making Ge$_{1-x}$Sn$_x$ interesting for high-speed electronics. An incorporation of Sn in the Ge lattice in a bottom-up synthesis should be carried out under kinetic control, because the binary phase diagram reveals the low equilibrium solubility of Sn in Ge (<1%). Aside from thin-film growth studies and postgrowth etching to prepare desired morphologies, reports on Ge$_{1-x}$Sn$_x$ nanostructures are emerging. Morphological control has been achieved creating core–shell Ge/Ge$_{1-x}$Sn$_x$ using Ge NWs as templates and non-template-based metal-seed-supported growth of Ge$_{1-x}$Sn$_x$ nanowires via gas-phase and solution-based synthesis. To date, the compositions vary in these reports on the growth of anisotropic Ge$_{1-x}$Sn$_x$ nanostructures with the highest values being in the range 9–13% Sn. Moreover, a transition to a semimetallic behavior with interesting applications can be expected when the Sn content is increased above 41%. Data confirming such high Sn concentrations in Ge$_{1-x}$Sn$_x$ with high crystallinity have only been rarely described in the literature with limited information about their actual homogeneity with maximum Sn contents of ~30%. The thermal stability of thin films with different composition is reported, but these reports do not

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usually cover higher tin contents >15%; the heat treatment is limited to a short time, e.g., by rapid thermal annealing, and the films are usually highly strained.58–60

This paper provides insight in the formation mechanism of anisotropic Ge1−xSnx nanostructures at temperatures as low as 140 °C leading to a Sn content of 28%, while the formation of α-Sn and its impact on the nucleation in this low-temperature process is elaborated. Two distinct compositions have been reliably synthesized with two different temperature profiles and pretreatment processes leading to Sn contents of ~17% and ~28% and without additional nucleation of branches or substructures. Thermal stabilities of these two alloy compositions are determined by variable-temperature X-ray diffraction (XRD) and subsequent microscopy studies. Our study reveals the strong influence of metallic Sn on the thermal stability of the Ge1−xSnx materials. Infrared (IR) absorption was used to characterize the materials’ properties and clearly shows the strong impact of direct bandgaps in the absorption spectra for both compositions.

EXPERIMENTAL SECTION

Chemicals. Butyl lithium, hexamethyldisilazane, SnCl2, 1,1,3,3-tetramethyldisiloxane, and GeCl4 were purchased from Sigma-Aldrich; All solvents were dried using standard procedures and stored over molecular sieve. All manipulations and syntheses have been conducted using Schlenk techniques or using an argon-filled glovebox. Li[N(Si(CH3)3)2] was prepared in hexane and purified by sublimation under reduced pressure. The GeCl4-dioxane complex was prepared according to a published procedure.41 The syntheses of Sn[N(Si(CH3)3)2]2 and Ge[N(Si(CH3)3)2]2 were prepared by a modified procedure published by Lappert et al. using a salt metathesis reaction.42

Dodecylamine (98%, Sigma-Aldrich) was kept for 2 h at 40 °C under dynamic vacuum and was distilled three times under reduced pressure. In the first distillation step high-molecular byproducts were separated. For the second and third distillation processes leading to Sn contents of ~17% and ~28% and without additional nucleation of branches or substructures.

Nanostructure Preparation. Ge NRs/NWs were grown in 10 mL glass cells (Anton Paar GmbH) at temperatures between 120 and 230 °C. The handling of the chemicals as well as the filling of the reaction vessels were carried out in a glovebox under stringent precautions against water.

In a typical experiment, 2 mL of dodecylamine was transferred in a glass cell for microwave synthesis. Dodecylamine was kept very close to the melting point. First, Sn[N(Si(CH3)3)2]2 and subsequently Ge[N(Si(CH3)3)2]2 were added to dodecylamine, and the glass cell was sealed with a Teflon-coated silicone cap. Independent of the ratio of Sn[N(Si(CH3)3)2]2 and Ge[N(Si(CH3)3)2]2, all samples prepared in this study have the same total concentration of 38 mM precursor to make a comparison possible. The vial was then transferred to the microwave reactor (Monowave 300; Anton Paar GmbH; frequency, 2.46 GHz) with an IR temperature control unit within 3 min. The precursor solution underwent a temperature program and was cooled down by a gas stream afterward. The synthesized structures were collected by adding toluene (3 mL) and subsequent centrifugation. The collected solid material was redispersed in toluene and centrifuged again to remove the dodecylamine. This step was repeated with ethanol another three times, and with toluene a further three times. The product was stored under ambient conditions in toluene.

Further information about the pretreatment of the precursor mixture for the synthesis of Ge1−xSnx NWs with 17% Sn is given in our previous paper.57 For the synthesis of Ge1−xSnx NRs with higher Sn content the following temperature programs were chosen: pretreatment 1 (PT1), (i) heat as fast as possible to 110 °C, (ii) cool down to 60 °C, (iii) hold for 10 min, (iv) heat as fast as possible to 140–160 °C, (v) hold temperature for 0–10 min, (vi) cool down to 55 °C; pretreatment 2 (PT2), (i) heat as fast as possible to 60 °C, (ii) hold temperature for 40 min, (iii) heat as fast as possible to 140–160 °C; (v) hold temperature for 0–10 min, (vi) cool down to 55 °C.

Nanostructure Characterization. The Ge1−xSnx NRs and NWs were analyzed using an FEIInspect F50 scanning electron microscope (SEM). The Ge1−xSnx NRs and NWs were deposited on lacey carbon copper grids (Plano) for transmission electron microscope (TEM) characterization. In this study, an FEI TECNAI F20 operated at 200 kV and equipped with a high-angle annular dark field (HAADF) STEM and EDX detector was used. The elemental maps were recorded using the EDAX TEAM package, and the quantification was calculated using the Ge(K) and Sn(L) signals. For the values included in the manuscript, inherent limits in accuracy related to EDX have to be considered (±0.5%). The images were recorded and treated using Digital Micrograph software. In situ heating experiments in the TEM were performed using a Gatan heating holder 652.

The X-ray diffraction (XRD) patterns were recorded on a PANalytical X-Pert PRO PW 3050/60 instrument in Bragg–Brentano geometry and Cu Kα radiation. High-temperature XRD (HTXRD) measurements were carried out using a PANalytical MPD Pro in grazing incidence mode with an incidence angle of 4° and Cu Kα radiation under hydrogen atmosphere. X-pert Highscore software was used for analysis of the measured data.

Transmission measurements were performed using the PerkinElmer Frontier FT-IR spectrometer in mid-IR mode. The spectra were acquired from 220 to 8000 cm−1, with a 4 cm−1 resolution, using 64 scans. A reference spectrum of the substrate was also acquired under the same conditions, thus allowing a determination of the NR and NW sample transmittance by rationing their spectrum against the one from the substrate. Then, the absorbance α (absorption coefficient times the thickness) was evaluated just by applying the logarithm (i.e., ln(T), where T is the transmittance). For the determination of the bandgap energy, we have employed the Tauc-plot method considering a direct bandgap of a material, which consists of a representation of (αhν)2 versus hν, with hν being the energy of the incident photons; the intersection of the linear trend at high energies with the abscissa axis will provide the bandgap energy of the analyzed material.

RESULTS AND DISCUSSION

Low-Temperature Growth Regime. The microwave synthesis in dodecylamine has been previously described for synthesis temperatures of 230 °C.33 A modified procedure has been developed to allow a controlled nucleation and growth of Ge1−xSnx nanostructures at temperatures as low as 140 °C requiring a certain pretreatment before the growth is initiated. Two pretreatment procedures (PT1, 10 min; PT2, 40 min) have been successfully applied and result in a material with identical morphology and composition (Figure S1). These investigations also allow us to identify different intermediate structures in the evolution of NRs and NWs.

The structural evolution at these low temperatures includes the formation of globular particles, which convert into teardrops, heterodimeric structures, and the formation of SnC leading to a Sn content of 28%, while the formation of α-Sn, structures at temperatures as low as 140 °C including a certain pretreatment before the growth is initiated.

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Li et al. has been also observed with other metal incorporation, such as observation of the large shift in the reflectance data observed here do not allow a definite assignment to either of the aforementioned triggers/processes for the phase transition from \( \beta \) to \( \alpha \)-Sn, but the incorporation of Ge is described \textit{vide infra} suggesting that the actual Ge content is responsible for the stabilization of this phase. Similarly, \( \alpha \)-Sn has also been observed with other metal incorporation, such as Li.

After 1.5 min, the first reflections associated with Ge\( x \)-Sn are evident, which are more prominent after prolonged decomposition because of the extension of the Ge\( x \)-Sn segment in the nanorods as can be expected from the SEM images (Figure 1c,d). The shift in the Ge reflections can be correlated to the concentration of Sn using the lattice constant of the cubic phase of tin (\( \alpha \)-Sn, 6.489 Å, JCPDS 00-005-0390), which is isostructural to cubic Ge (5.658 Å), according to Vegard’s law. This calculated value is quite accurate for structures where no strain from a substrate has to be taken into account; however, for highly accurate determination of the composition of surface-bound epitaxial layers, a small deviation is corrected by the bowing parameter which is highly dependent on the literature reports.

In an earlier report, we quantified the Sn concentration via EDX using the Sn(K) line, which leads to an underestimation of the actual Sn content in Ge\( x \)-Sn NWs. In addition, the large variation of the related Raman shift in the literature on thin epitaxial films can be misleading.

TEM images of NRs clearly show a quasi-hemispherical segment and the NR body with different diffraction contrast (Figure 2a). Focusing on the NR body by high-resolution (HR)TEM reveals the high crystallinity, which is also illustrated in the sharp fast Fourier transformation (FFT) pattern of Figure 2a. The local Sn concentration in the Ge\( x \)-Sn, NRs has been evaluated using scanning transmission electron microscopy (STEM) energy dispersive X-ray spectroscopy (EDX) mapping using the Sn(L) and the Ge(K) line for quantification. The elemental mapping reveals the homogeneous distribution of Sn in the Ge matrix without any sign of clustering in the NR body (Figure 2b).

The Ge\( x \)-Sn NRs grown at 140 °C show two distinct sites of Sn enrichment located at both extremes on the NRs. The bigger globular part is located at the growth front of the NRs as described before for NWs grown at 230 °C, while a small section of Sn enrichment is located at the nucleation site. This is a general phenomenon for these NRs derived at 140 °C as illustrated in additional STEM-EDX mappings of NRs in the Supporting Information (Figure S2). A transition zone of slightly higher Sn content (~32%; 100–150 nm transition zone) can be found between this Sn-rich area and the constant Ge\( x \)-Sn composition of surface-bound epitaxial layers, a small deviation is corrected by the bowing parameter which is highly dependent on the literature reports.

At slightly higher growth temperatures of 160 °C, the aforementioned Sn-rich particle at the nucleation site can completely phase separate and act as a second growth seed for a thinner NR as shown in Figure 3. This thinner NR has a diameter of ~50 nm and the same composition as the thicker nanorod (\( \Phi = 210 \) nm) with 26.5% Sn, while the initial nucleation area shows a higher Sn percentage (32%). This comparison illustrates a diameter-independent composition for NR diameters of 50–250 nm at these low temperatures and rather epitaxial growth on an initial seed with partial relaxation and formation of the most stable composition at the given growth conditions.

Without the pretreatment, the nanostructures tend to form NRs with secondary, “parasitic” structures protruding from the initial nucleation site, and uncontrolled nucleation of undefined, branched structures as illustrated in Figure S3 are...
observed. In a separate set of experiments, the dodecylamine was substituted by n-octylamine, and the growth was repeated under identical conditions with the same pretreatment at temperatures of 130–160°C. The elongated structures contain an even higher Sn content in the NR body (32.1 ± 0.5% Sn according to EDX, Figure S4) and could be interesting for applications taking advantage of semimetallic properties; however, the structures tend to form secondary nucleation centers at the surface leading to uncontrolled branching (especially at early stages of the Ge$_{1-x}$Sn$_x$ crystal formation with a nominal Sn content of 35.6%), which can be related to different decomposition rates of the formed metallorganic intermediates and correlated changes in the nuclei formation and growth kinetics. The formation of the secondary nucleation sites can be most likely attributed to thermal instability of the Ge$_{1-x}$Sn$_x$ composition as described vide infra.

According to the results observed here, a growth mechanism for these NRs growing at 140°C is proposed (Figure 4a). The pretreated precursor mixture contains homometallic Sn species leading to the formation of β-Sn particles as a first step. The β-Sn particles contain ≤0.4% Ge averaged over the whole particle according to STEM-EDX analysis. Figure S5a shows the Ge predominantly accumulated at the Sn surface, while the majority of Ge can be expected to be distributed within the β-Sn particle at elevated temperatures and separation that occurs upon cooling. These globular β-Sn particles are converted to teardrop shaped α-Sn by additional gradual incorporation of Ge that stabilizes this cubic Sn phase. The α-Sn phase is expected to form via solid diffusion requiring a critical Ge concentration (~0.7–1.0% according to EDX analyses of several particles similar to the one shown in Figure S5b). A critical parameter at this stage is the initially slow rate of Ge precursor decomposition leading to a gradual increase in Ge content. While the Ge concentration must be high enough for the conversion to α-Sn, the local concentration should also be low enough to avoid an initial nucleation of a Ge$_{1-x}$Sn$_x$ particle. A complete or a partial conversion to the α-Sn particles observed. In a separate set of experiments, the dodecylamine was substituted by n-octylamine, and the growth was repeated under identical conditions with the same pretreatment at temperatures of 130–160°C. The elongated structures contain an even higher Sn content in the NR body (32.1 ± 0.5% Sn according to EDX, Figure S4) and could be interesting for applications taking advantage of semimetallic properties; however, the structures tend to form secondary nucleation centers at the surface leading to uncontrolled branching (especially at early stages of the Ge$_{1-x}$Sn$_x$ crystal formation with a nominal Sn content of 35.6%), which can be related to different decomposition rates of the formed metallorganic intermediates and correlated changes in the nuclei formation and growth kinetics. The formation of the secondary nucleation sites can be most likely attributed to thermal instability of the Ge$_{1-x}$Sn$_x$ composition as described vide infra.

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can be expected under growth conditions with the possibility of coexisting Sn phases. Unfortunately this growth stage could not be fully investigated because of potential material modification during the cooling of the material in the microwave process and no possibility of rapid quenching with the used equipment. However, the presence of an α-Sn phase is important for the formation of NRs with such a high Sn content as discussed below.

Increased thermal input accelerates the decomposition kinetics of the precursor species, and thus no α-Sn can be formed because of a quick oversaturation of the Sn particle and the subsequent nucleation of a Ge₁−ₓSnₓ crystal (similar to a nucleus observed in Figure S5c formed at 180 °C). In addition, increased growth temperatures reduce the probability of an α-Sn phase formation. This indicates already that the exclusive nucleation/formation of the Ge₁−ₓSnₓ phase formation. This indicates already that the exclusive nucleation/formation of Sn-rich side of a phase map and the assumption of a peritectoidic nucleation during the layer formation. This suggests that the exclusive nucleation/formation of the Ge₁−ₓSnₓ phase formation.

Further reaction at the growth temperature of 140 °C leads to the observation of a typical quasi-hemispherical β-Sn part in Ge₁−ₓSnₓ/Sn heterodimers. These structures can be formed by a destabilization through an ongoing supersaturation of a fully developed α-Sn teardrop with formation of an associated Ge₁−ₓSnₓ nucleus and a subsequent collapse of the crystal structure by diffusion processes. Another possibility that should not be neglected would be the nucleation of Ge₁−ₓSnₓ in a possible Sn phase mixture with the α-Sn acting as template. Subsequent growth of the Ge₁−ₓSnₓ segment proceeds through decomposition of more Ge-rich precursor species after the initial nucleus formation and appears to be a quick process according to Figure 1. The growth of the highly crystalline metastable Ge₁−ₓSnₓ with this extremely high Sn content should be facilitated at low temperature because of reduced Sn incorporation at increasing temperatures. The α-Sn phase can act as a template for epitaxial growth of highly Sn-rich Ge₁−ₓSnₓ (mismatch to cubic Ge of ~ 15% for pure α-Sn) facilitating crystal growth of the thermodynamically unfavorable composition. Indication of a formation of Ge₁−ₓSnₓ without any tensile strain and the most favorable constant composition at a given parameter set are observed ~100–150 nm from the nucleation seed where a constant composition is observed along the NRs. Figure S5d–f in the Supporting Information illustrates different stages of the NR evolution from the formed heterodimers with two distinct Sn areas present in all the different stages after the Ge₁−ₓSnₓ segregation.

We do not consider the generally accepted solute trapping at step edges during the nanowire growth to be the major driving force for the formation of Ge₁−ₓSnₓ at these low temperatures as suggested for other metastable compositions in NWs. A slightly modified process should be at play because the step-edge-based growth typically also suggests that the nanowire growth can proceed with the successive addition of bilayers through a step flow process and oscillating supersaturation during the layer formation. The Ge₁−ₓSnₓ NRs and NWs grown in these microwave processes usually do not show a sharp interface with a specific atomic plane terminating the semiconductor segment at the interface to the metal particle, and thus the model might not be fully applicable.

These suggestions on the growth mechanism are based on the morphologies and phases observed after the cool-down procedure and without information on processes occurring in situ during the growth. Thus, the information about the initial
stage before the Ge$_{1-x}$Sn/Sn heterodimer formation is not entirely clear and might require more experiments with modified setups allowing either in situ monitoring or rapid quenching.

The described growth regime differs from the 230 °C samples, because these 230 °C derived NWs do not show additional secondary growth at the nucleation site nor a remaining Sn particle. Moreover, the different pretreatment leads to a change in the ratio of the precursor species in the mixture. Long-term treatment for the growth at 230 °C does not lead to nucleation in the heating step similar to the here-described scenario for the 140 °C nucleation. The structure formation for the 230 °C growth exclusively takes place at the higher-temperature regime which can be illustrated by different growth stages/lengths of these NWs. The structures are only observed after the high-temperature growth cycle, and thus the formation at lower temperatures in these specific sets of experiments can be excluded.

Observations described above for the growth of Ge$_{0.67}$Sn$_{0.33}$ at 140 °C do not correlate with the conventional Ge/Sn phase diagram (Figure S6). A traditional binary phase diagram is obtained under thermodynamic equilibrium conditions. Therefore, such diagrams are not suitable to explain a kinetically driven formation of metastable phases, such as Ge$_{1-x}$Sn$_x$ with high Sn contents, which differ significantly from the equilibrium composition. However, we coin a term for such a descriptive or schematic representation as a “phase map” that includes some kinetic effects/phase compositions. For a phase map as presented and suggested herein, we have to consider phases and compositions formed under a specific parameter set. In this specific case, the formation of Ge$_{1-x}$Sn$_x$ with a metastable composition as well as the other metastable, or simply not under regular conditions, observable α-Sn phase should be discussed.

According to the phase evolution encountered here for Sn depending on the Ge content, a representation of the Sn-rich side of the phase map should include a peritectoidic reaction (α-Sn ↔ α-Ge + β-Sn; a solid–solid reaction below 180 °C; Figure 4b). However, the formation of this α-Sn phase relies on the incorporation of Ge atoms in the initial β-Sn lattice without segregation or Ge nucleus formation. This incorporation in the solid phase can be supported by the high mobility of surface atoms of low-melting metals such as Sn and has a stabilizing effect on the crystal phase. One can anticipate this peritectoidic α-Sn phase being a thermodynamically stable phase that is simply not being observed in the conventional heating and cooling experiments that are used for conceiving a phase diagram because of the very slow reaction rates of two solid phases being β-Sn and α-Ge. Providing the Ge in atomic form speeds up this process, and we can observe the phase in this study. In addition, energetic considerations suggest that there is only a small energy difference between the two Sn phases at the growth temperature of 140 °C. Higher Ge contents will not be incorporated in α-Sn, and α-Ge will nucleate. More reliable statements on α-Sn being thermodynamically stable or simply being a metastable phase would require more elaborate calculations, which also consider the high energy gain upon α-Ge crystal formation.

The existence of a miscibility gap between the two isostructural α-Sn and α-Ge phases showing no solid solubility over the full range of compositions could be related to early predictions by Hume-Rothery. Stability issues can be related to the size differences of Sn and Ge, which are in this case ~15% representing a threshold value between the existence of solid solutions over a wide composition range and the occurrence of a large miscibility gap associated with low solubility <1% as observed in the Ge/Sn phase diagram. A threshold for maximum Sn composition of the stable Ge$_{1-x}$Sn$_x$ alloy should be dependent on growth kinetics and growth temperature as schematically illustrated on the Ge-rich side in the phase map in Figure 4c. Our phase map suggests the formation of the α-Sn phase with a miscibility gap toward an α-Ge phase, representing the metastable Ge$_{1-x}$Sn$_x$ solid solution with compositions associated with growth kinetics and growth temperature. The purple, blue, and dashed lines represent the maximum Ge$_{1-x}$Sn$_x$ composition obtained for three specific parameter sets. Since growth kinetics are very important during the Ge$_{1-x}$Sn$_x$ crystal growth, e.g., with a solute-trapping model in the case of nanowire growth, a higher or lower growth rate could result in a material with higher or lower Sn content. At the same time, a temperature-dependent factor has to be considered for the phase map with a known tendency of diminishing Sn incorporation in Ge$_{1-x}$Sn$_x$ with increasing temperature. The isothermal line at 140 °C in Figure 4c traverses the schematic purple and blue transition lines of maximum Sn content in the Ge$_{1-x}$Sn$_x$ alloy. These crossing points represent the composition in the Ge$_{0.67}$Sn$_{0.33}$ NR and Ge$_{0.66}$Sn$_{0.34}$ NWs for the same set of parameters (pretreatment and temperature profile) but different solvent and ligands of the precursors as described vide supra.

**Thermal Stability of Ge$_{1-x}$Sn$_x$ NRs and NWs.** For an investigation into the stability of anisotropic Ge$_{1-x}$Sn$_x$ structures with very high Sn content (17% and 28% as starting compounds), variable high-temperature (HT) XRD experiments in the temperature range 120–500 °C have been performed. To the best of our knowledge there is no report available on the thermal stability of Ge$_{1-x}$Sn$_x$ material, which is also in contact with a metallic phase.

In a first set of experiments, Ge$_{0.63}$Sn$_{0.37}$ NWs have been prepared as described before, and a thin film of the NWs has been heated while recording the XRD patterns. The temperature is increased in 10 °C steps and kept at the temperature for 10 min before the measurement is started, which takes 20 min. Therefore, changes over time can have an uncertainty of ~10 °C if the effects are only observed after an initial delay. The β-Sn reflections can be considered as an internal standard until this phase melts at ~230 °C. The shifted Ge reflections due to the enlarged unit cell upon the incorporation of Sn have to be considered for the stability tests since the shift is directly related to the composition by Vegard’s law. Figure 5 shows no changes in the position of the reflections up to temperatures of 190 °C. At 200 °C the reflection broadens toward higher angles, and a new composition with lower Sn content is observed (~6% Sn). With a further increase of temperature, a continuous decrease of Sn content is observed, and at 500 °C only 3.5% Sn is left in the structure. The Ge$_{0.66}$Sn$_{0.34}$ NWs show a broad peak at ~170 °C which shifts to ~180 °C for the Sn growth seed attached NWs.

The Ge$_{0.67}$Sn$_{0.33}$ NRs with attached Sn growth seeds have been investigated as described before in the temperature range 120–500 °C (Figure 6a). No changes in the XRD patterns are observed up to 150 °C. A shoulder of the Ge (111) reflection evolves toward higher 2θ angles at 160 °C, and the signal...
clearly splits at 170 °C into two reflections with a new composition of Ge0.90Sn0.10 and the original Ge0.72Sn0.28 composition. At temperatures of 180–190 °C a shoulder representing the higher tin concentration is still present with diminishing intensity while only one reflection representing ~6% Sn remains at 210 °C. This composition is very close to the value observed for the Ge0.83Sn0.17 NW starting material containing ~6% at the same temperature. An identical value of 3.5% Sn is observed for both starting compounds after temperature treatment at 500 °C for 30 min and prior ramping as described for all variable-temperature experiments. The 3D representation of the significant temperature window is illustrated in Figure 6b and shows in addition to the shift of the Ge1−xSnx (111) reflection an increase in the β-Sn content, which can be expected upon thermally induced spinoidal decomposition of crystalline Ge1−xSnx in a material Ge1−ySn with lower Sn content (x > y) and the segregation of Sn. Since these relevant conversion temperatures are below the melting point of Sn, a solid diffusion can be expected.

The onset of thermal decomposition is represented by the appearance of a shoulder of the Ge (111) reflection toward higher angles starting at temperatures of 160 °C in Figure 6. However, the as-prepared Ge0.72Sn0.28 composition decomposes slowly at a static temperature of 140° (Figure 6c, and Figure S9) held for 6 h. The onset of the decomposition requires time, and since the temperature is only held for 30 min at each temperature in the variable-temperature study in Figure 6a, this effect is only observed at higher temperatures. An unchanged composition and thus associated stability of Ge0.77Sn0.23 with Sn seeds attached is observed at 120° for 6 h as illustrated in Figure 6c, and Figure S10. The changes in the XRD pattern associated with a material conversion to Ge1−xSnx with lower Sn content in the isothermal heating experiments shows an exponential decay of the Ge0.77Sn0.23 starting compound after an initial incubation period. An example of this behavior is shown in Figure S11 for a 6 h heating cycle of as-grown Ge0.77Sn0.23 NRs at 150 °C.

We assign the peak splitting to the destabilization of the Ge0.77Sn0.23 and related gain of lattice energy by the formation of a more thermodynamically favorable composition, which requires additional energy for the conversion by diffusing species. Hence the decomposition and rearrangement of the Ge lattice should occur at lower temperatures in the Ge0.77Sn0.23 sample because approximately every fourth atom in the cubic lattice is a Sn atom. After the splitting of the signal and temperatures above 160 °C the subsequent segregation of Sn is
a gradual effect. Theory predicts that the number of defects with Sn in octahedral configuration increases with growth temperature, and therefore the alloy should be less stable because of Sn in 6-fold coordination, thus contributing to Sn segregation. However, extended X-ray absorption fine structure investigations on Ge$_{1-x}$Sn$_x$ with $x_{max} = 13\%$ illustrate that Sn preferentially resides on substitutional sites, and no indices of this 6-fold coordination are observed. In addition, the low synthesis temperature and the well-matched values for XRD and EDX results presented here should account for the low synthesis temperature and the well-matched values for temperature stability of the alloy should be less stable compared to material with lower Sn content could be related to an epitaxial growth of Ge$_{1-x}$Sn$_x$ (y < x) by redeposition from the migrating β-Sn segment (with increasing volume fraction observed in the XRD studies vide supra).

Moreover, the onset of the diffusion process seems to originate exclusively at the bigger Sn particle, which points toward the importance of the initial Sn/Ge$_{1-x}$Sn$_x$ interface for this low-temperature structural/compositional conversion process being initiated.

It is noteworthy that all these processes take place below the melting point of Sn (232 °C). Ge$_{0.72}$Sn$_{0.28}$ NRs treated in the TEM at 220 °C for ~10 min and prior diffusion at 200 °C show preferential Sn enrichment at the two extremes (Figure 7 g,h), while treatment for 20 min at 180 °C in squalane shows more large patches of Sn-enriched regions between the extremes (Figure 7i). The NRs do not show distinct morphological changes in the SEM images before and after the temperature treatment (Figure S11c,d). TEM images of these NRs also show predominantly two darker segments at the extremes due to a different diffraction contrast, which have not been observed in the as-grown samples. More examples for the formation of phase-separated Sn patches are shown in Figure S11e−g, but fewer of the obvious Sn regions between the two extremes are observed in STEM-EDX images when the samples have been treated at higher temperatures. The reason for shape...
 retention could be either the surface termination with amino functionalities, a slight surface oxidation layer, or simply and most likely the bulk conversion/diffusion at these temperatures below the melting point of the elements involved. STEM-EDX images help to identify the segment composition. The Ge$_{1-x}$Sn$_x$ segment is not as defined anymore, suggesting also Ge diffusion and rearrangement processes (Figure 7g–i). The aforementioned mass transport is most likely initiated by a solution/redeposition process involving the diffusing β-Sn precipitate. The redeposited material contains less Sn in the Ge host structure; therefore, the process is driving toward the thermodynamically favored Ge-rich lattice, and a gain in lattice energy during the process can be expected. The redeposition/recrystallization of Ge$_{1-x}$Sn$_x$ ($x > y$) is made evident and most obvious by comparing the Ge mapping after the temperature treatment with the initial distribution (Figure S12e–h). A striking difference is visible at the initial nucleation site, where no Ge can be found after this process, and at the sites of the Sn patches along a NR where the Ge is completely replaced by Sn.

Differences in thermal stability of these structures when compared to other studies on Ge$_{1-x}$Sn$_x$ should be mentioned. The most important difference is the presence of the Sn metal, which can dissolve and recrystallize Ge$_{1-x}$Sn$_x$ while a metal first has to be formed when pure Ge$_{1-x}$Sn$_x$ decomposes and Sn segregates. This process of spinoidal decomposition requires a partial breakdown of the crystalline structure, and thus more thermal energy has to be provided to overcome the lattice energy. Thus, a removal of the Sn seed material from the NRs and NWs by exposure to 5% hydrochloric acid for 5 min should lead to increased thermal stability. Figure S13 compares variable-temperature XRD results of Ge$_{0.72}$Sn$_{0.28}$ NRs with and without the Sn seeds demonstrating the expected increased thermal stability with temperatures up to ~220 °C without decomposition, which is ~70 °C above the onset of a material conversion in the presence of Sn. A similar measurement using Ge$_{0.83}$Sn$_{0.17}$ NWs illustrates the same effect and stability up to 250 °C (versus ~190 °C with Sn seeds in Figure S, and for comparison without Sn in Figure S14). Temperature stability for an extended time is usually observed ~30 °C below these values as shown vide supra. In addition, the results presented here can nicely explain the low-temperature crystallization of amorphous Ge$_{1-x}$Sn$_x$ layers from a laser-annealed region forming highly crystalline Ge$_{1-x}$Sn$_x$ material. This process resembles metal-induced crystallization of Ge occurring at higher temperatures, but leads to a metastable material composition.

Bulk Ge exhibits a fundamental indirect bandgap of 0.67 eV and a direct gap at 0.80 eV. Incorporation of Sn in the Ge crystal reduces both energy gaps, but the direct one to a larger degree than the indirect. Therefore, a direct semiconductor material is expected for the high Sn contents described herein. For a demonstration of the optical bandgap of the not thermally degraded Ge$_{1-x}$Sn$_x$ material, Figure 8 shows the direct bandgap of Ge$_{0.72}$Sn$_{0.28}$ NRs and Ge$_{0.83}$Sn$_{0.17}$ NWs described herein. From IR absorption experiments, a Tauc plot was prepared to determine the bandgap energy. A Tauc plot is a common way to determine the optical bandgap of semiconductors.

A determination of the bandgap in the material is achieved by plotting $(ahv)^n$ versus $hv$ and relating the factor $n$ to an indirect ($n = \frac{1}{2}$) or direct ($n = 2$) bandgap and the absorption coefficient ($\alpha$). Approximate bandgaps of 0.29 eV for Ge$_{0.72}$Sn$_{0.28}$ NRs and 0.40 eV for Ge$_{0.83}$Sn$_{0.17}$ NWs were determined by extrapolating a tangential line from the linear portion of the Tauc plot to the abscissa. The direct bandgaps observed in these NRs and NWs are far below the usual bandgaps of Ge, which is expected for a successful incorporation of Sn in Ge$_{1-x}$Sn$_x$ above ~9% for a relaxed material and could be an indication that these NRs and NWs are indeed direct bandgap materials. More detailed physical characterization of the presented materials is out of the scope of this paper.

■ CONCLUSIONS

A low-temperature growth at 140 °C for the formation of Ge$_{1-x}$Sn$_x$ NRs with a very high Sn content of 28% has been established. The typical low-temperature α-Sn phase has been observed during the formation of the NRs, and all the anisotropic structures remained a Sn-rich region at the nucleation site, which cannot be observed at nucleation at higher temperatures. Therefore, we propose a growth mechanism for this particular set of parameters that is based on a Ge-stabilized α-Sn intermediate. Moreover, the thermal stability of two sets of NRs and NWs with different Sn content has been investigated via XRD, and the data reveal decomposition at a low temperature that has to be considered for the determination of their physical properties as well as the potential device operation. In addition, the low-temperature decomposition of Ge$_{1-x}$Sn$_x$ appears to be related to a solid diffusion of Sn as observed as mobile sections with different diffraction contrast during in situ TEM annealing experiments. The segregated Sn accumulates at low temperatures at the extremes of NRs and also as patches in between. The continuous release of Sn accompanied by the formation of crystalline Ge$_{1-x}$Sn$_x$ with lower Sn content and also spatial distribution of the elements suggest dissolution and recrystallization events facilitated by diffusing Sn. Removal of the metallic Sn from the Ge$_{1-x}$Sn$_x$ results in enhanced stability toward thermal decomposition by ~70 °C for Ge$_{0.72}$Sn$_{0.28}$ NRs and ~60 °C for Ge$_{0.83}$Sn$_{0.17}$ NWs. A direct bandgap in the starting materials with such high Sn contents has been demonstrated via absorption experiments and the use of graphical illustration in Tauc plots.


**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.7b03969.

Additional SEM, TEM, EDX, and XRD data (PDF)

Video S1: TEM images obtained under temperature treatment using Ge_{0.72}Sn_{0.28} NRs showing different steps in the phase segregation process (AVI)

Video S2: Additional NR imaging (AVI)

Video S3: Additional NR imaging (AVI)

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The authors declare no competing financial interest.

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**REFERENCES**


(7) Lu Low, K.; Yang, Y.; Han, G.; Fan, W.; Yeo, Y.-C. Electronic band structure and effective mass parameters of Ge_{1-x}Sn_{x} alloys. *J. Appl. Phys.* 2012, **112**, 103715.


(13) Pham, T. N.; Du, W.; Conley, B. R.; Maretjis, J.; Sun, G.; Soref, R. A.; Tolle, J.; Li, B.; Yu, S. Q. Si-based Ge0.95Sn0.05 photodetector with peak responsivity of 2.85 A/W and longwave cutoff at 2.4 μm. *Electron. Lett.* 2015, **51**, 854.

(14) Tseng, H. H.; Wu, K. Y.; Li, H.; Mashanov, V.; Cheng, H. H.; Sun, G.; Soref, R. A. Mid-infrared electroluminescence from a Ge/Ge0.92Sn0.08/Ge double heterostructure p-n diode on a Si substrate. *Appl. Phys. Lett.* 2013, **102**, 182106.


