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Strained $\text{Ge}_{1-x}\text{Sn}_x$ thin films have recently attracted a lot of attention as promising high mobility or light emitting materials for future micro- and optoelectronic devices. While they can be grown nowadays with high crystal quality, the mechanism by which strain energy is relieved upon thermal treatments remains speculative. To this end, we investigated the evolution (and the interplay) of composition, strain, and morphology of strained $\text{Ge}_{0.94}\text{Sn}_{0.06}$ films with temperature. We observed a diffusion-driven formation of Sn-enriched islands (and their self-organization) as well as surface depressions (pits), resulting in phase separation and (local) reduction in strain energy, respectively. Remarkably, these compositional and morphological instabilities were found to be the dominating mechanisms to relieve energy, implying that the relaxation via misfit generation and propagation is not intrinsic to compressively strained $\text{Ge}_{0.94}\text{Sn}_{0.06}$ films grown by molecular beam epitaxy. Published by AIP Publishing. [<http://dx.doi.org/10.1063/1.4961396>]

I. INTRODUCTION

The materials library used in semiconductor processing and devices has been expanded enormously over the last decades to satisfy society's increasing demand for faster, cheaper, and smarter devices. Recently, (Si)GeSn alloys have attracted a lot of attention as a tailored Sn, Ge (and Si) stoichiometry permits to further boost charge carrier mobility¹ and to tune type (indirect to direct) and magnitude of the energy band gap² via strain engineering. To date, high quality crystalline (Si)GeSn strained thin films can be grown on various substrates (Si, Ge, virtual Ge) with Sn concentrations above the equilibrium solid solubility (>1 at. % Sn³) relying on the advanced film growth methods such as Chemical Vapor Deposition (CVD)⁴⁻⁶ or Molecular Beam Epitaxy (MBE).⁷⁻¹¹ However, thermal stability of these metastable films is low, particularly for high Sn content, and thus sustaining their physicochemical and hence their electrical and optical properties during further processing steps remains a major challenge.

Thermal treatments of (supersaturated) strained $\text{Ge}_{1-x}\text{Sn}_x$ films commonly lead to compositional instabilities caused by phase separation as well as precipitation and surface segregation of Sn.^{10,12-16} This phenomenon is attributed to thermally enhanced diffusion, the lower melting temperature of Sn compared to Ge, and/or the low solubility of Sn in Ge. Morphological instabilities such as the excavation of surface trenches^{13,14,16} or the formation and self-assembly of Sn wires¹⁷ have also been reported. Yet, it remains unclear

whether these surface modifications are a kinetic pathway for phase separation and strain relaxation,¹³ since Chen *et al.*¹⁴ did not observe any significant changes in the macroscopic strain level and only a minor reduction in the Sn concentration of the $\text{Ge}_{1-x}\text{Sn}_x$ film. Indeed, several authors^{9,12,18} argue that the dominating mechanisms of strain relaxation in $\text{Ge}_{1-x}\text{Sn}_x$ alloys appear to be the formation of misfit dislocations rather than compositional or morphological instabilities, similar as in other group-IV alloys.¹⁹

Clearly, we lack a comprehensive picture on the thermal stability and relaxation mechanisms, including both compositional and morphological changes in strained $\text{Ge}_{1-x}\text{Sn}_x$ films. At present, we miss a detailed characterization of these instabilities as well as their evolution with temperature, which is, however, a stepping stone to reveal the underlying atomic processes. It goes without saying that a fundamental understanding of these atomic processes is urgently required for thin film deposition and processing and hence to achieve further progress in this field of research, as was also recently highlighted in a review on GeSn transistor research.²⁰ To this end, we investigated the thermal stability and relaxation mechanisms in thin $\text{Ge}_{0.94}\text{Sn}_{0.06}$ films grown by MBE. This paper presents the film compositional and morphological evolution with temperature and links these observations to the strain in the layer. It describes our findings on (i) the general film behavior and properties in view of strain and compositional changes; (ii) the formation of individual surface structures; and (iii) the self-assembly of these structures into trenches and circular patterns.

II. EXPERIMENTAL

$\text{Ge}_{0.94}\text{Sn}_{0.06}$ films were grown by low-temperature (150°C) MBE on cleaned Ge(001) substrates as described in more detail in Refs. 21 and 22. The Sn concentration ($\sim 6\%$) and the layer thickness (40 nm or 75 nm) were measured by Rutherford backscattering (RBS) (data not shown). Good crystalline quality, with Sn atoms residing on substitutional lattice sites, was verified in the 40 nm film by X-ray diffraction (see Figure 3(a)) and channeling-RBS measurements (data not shown). For the latter, the Sn minimum yield amounts to $\sim 14\%$ in the as grown 40 nm film (measured along the [110] axis of the GeSn film). The film surface is very smooth, with a root-mean-square (rms) surface roughness < 0.4 nm (see Figure 6). The crystal quality is lower in the as grown 75 nm thick film, which exhibits a cross-hatch morphology on the surface before annealing. Annealing was performed under ultra-high vacuum conditions for 30 min in a temperature range of 300 – 800°C .

The samples were analyzed with respect to their *chemical composition and Sn-content* using scanning Auger electron spectroscopy (AES), reference-free grazing-incidence X-ray fluorescence analysis (GIXRF), as well as high-resolution reciprocal space mapping (RSM-XRD) around the (224) reflection. To ensure accuracy for the AES measurements, two GeSn samples without heat treatment (1.1 at. % Sn and 5.7 at. % Sn) were used for calibration. The Sn content (and layer thickness) in these reference samples was verified by RBS measurements (data not shown). AES quantification was based on the Sn/Ge ratio as determined from the peak-to-peak height of the Sn *MN5* and Ge *LM3* Auger lines. 2–3 scans were averaged for the data shown. The uncertainty was estimated to be around 10% to account for the measurement and quantification uncertainty. If local concentration variations exceeded this uncertainty, the error bars indicate the standard deviations between several scans. The AES beam size is a few hundred nanometers, enabling direct concentration measurements on surface features that are larger than that.

The GIXRF experiments were conducted in the laboratory of the Physikalisch-Technische Bundesanstalt (PTB) at the synchrotron radiation facility BESSY II using an experimental arrangement for reference-free X-ray spectrometry.²³ Measurements were performed at the PTB's four-crystal monochromator (FCM) beamline using an excitation energy of 5 keV (9° incidence angle). The use of calibrated instrumentation²⁴ allows to deduce the Sn mass deposition in the sample from the measured fluorescence intensities.²⁵

Besides the Sn composition, RSM-XRD yields information about the in- and out-of plane lattice spacing and *strain* in the GeSn film. The composition and strain were deduced²⁶ by taking into account the elastic moduli of Ge ($C_{11} = 128.5$ GPa, $C_{12} = 48.3$ GPa, and $C_{44} = 66.8$ GPa (Ref. 27)) and Sn ($C_{11} = 72.5$ GPa, $C_{12} = 29.7$ GPa, $C_{44} = 29.9$ GPa (Ref. 28)). Note that a fully *strained* GeSn layer exhibits the same in-plane lattice constant as the Ge substrate, while a fully *relaxed* GeSn layer shows an in-plane lattice constant that is increased accordingly (in function of the Sn content). Additional qualitative information about the molecular bonding structure in the layer was gained by microscopic Raman measurements using

a He-Ne laser (633 nm) with a power of ~ 0.1 mW and a laser spot size of ~ 2 μm diameter ($\times 50$ objective). Sn diffusion was traced by secondary ion mass spectrometry (SIMS) using a 1 keV O_2^+ primary ion beam at 41° incidence angle.

Morphological changes were recorded with an atomic force microscope (AFM) using the Nanotec WSxM software²⁹ for data analysis, optical dark field microscopy, and cross-sectional transmission electron microscopy (TEM). To obtain combined information about surface topography and composition, we performed near-field infrared (IR) imaging on a commercial scattering type scanning near-field optical microscope (SNOM) with the AFM operated in tapping mode.^{30,31} For the measurements, Au-coated silicon-based AFM cantilevers with typical tip diameter below 50 nm were used. The high-resolution images in the IR range were recorded using a tunable CO_2 gas laser. In order to perform background-free near-field imaging pseudo-heterodyne, interferometric detection of the backscattered light combined with subsequent demodulation of the detector signal at higher harmonics of the cantilever's tapping frequency was applied.³²

III. RESULTS AND DISCUSSION

A. General film behavior and properties: Strain and compositional changes

We will first discuss the thermally induced compositional instabilities and strain relaxation in the 40 nm GeSn film, as this knowledge will be conducive to the discussion on the morphological instabilities observed. The film composition was quantified *ex-situ* after each annealing step using different characterization methods, i.e., AES, GIXRF, SIMS, and RSM-XRD. The result of this analysis is summarized in Figure 1 and Table I. This approach allows for tuning the information depth and hence to differentiate between: (1) the *surface* composition of the film and surface features, respectively (see the inset of Figure 1 and discussion below) (AES); (2) the *total* amount of Sn in the layer (GIXRF and SIMS); and (3) the *substitutional* Sn content (RSM-XRD). The latter technique also yields information on the lattice parameter and, consequently, the degree of strain relaxation (R) as well as the in-plane and out-of-plane strain energy, as summarized in Table I.

The film composition and lattice structure are unaltered for temperatures until 500°C as compared to the as grown film with Sn atoms remaining in substitutional lattice sites (Figure 1(a), triangle). Likewise, the Sn SIMS profiles of the as grown and annealed film show identical signal intensities and slopes (Figure 1(b)), implying that the Sn concentration and distribution in the GeSn film remain unchanged. A comparable thermal stability has been reported in Refs. 5, 12, and 14. With increasing temperature (600°C), a minor reduction in the substitutional Sn content is detected by RSM-XRD measurements. This can be attributed to the formation of Sn-enriched (12 at. % Sn) precipitates (Figure 1(a), inset) and a marginal bulk in-diffusion of Sn, the latter being revealed by SIMS measurements (Figure 1(b)). Yet, the ^{120}Sn signal intensity in the GeSn film still equals that of the as grown layer. Hence, the amount of Sn diffused

FIG. 1. (a) Evolution of the Sn content with annealing temperature measured at the film surface (circles), the island surface (squares), on substitutional lattice sites (triangles) and in the complete layer (stars) of a 40 nm Ge_{0.94}Sn_{0.06} film. Note that the AES measurements distinguish between the film surface and the surface of an island as shown in the inset. (b) Sn profiles of the as grown and annealed GeSn films determined by SIMS measurements.

into the Ge substrate is very low, in agreement with the RSM-XRD measurements. In the bonding structure, no changes can be discerned either. The Raman measurements (Figure 2) show no reduction in the peak intensity of the

Ge-Sn ($\sim 262 \text{ cm}^{-1}$) and the Sn-Sn-like vibrational modes ($\sim 184 \text{ cm}^{-1}$)^{28,30} after annealing to 400 °C, 500 °C, or 600 °C, implying a comparable bonding configuration and amount of Ge-Sn (Sn-Sn) bonds as in the as grown film. Note that the peak observed at low energy was previously assigned³³ to a mixture of Sn-Sn longitudinal optical (LO) and Ge longitudinal acoustic (LA) phonon modes and hence does not solely arise from Sn-Sn bonds. The strongest Raman signal is assigned to Ge-Ge LO modes,^{33–35} originating from both the GeSn layer and the Ge substrate. We estimate the probed depth when using 633 nm laser light to be approximately 77 nm, i.e., larger than the film thickness, based on a linear interpolation of the data given in Ref. 36 for pure Ge. To quantify the exact contribution of the Ge substrate to the Ge-Ge mode, we require the Raman scattering cross-section and photoabsorption coefficient for Ge_{0.94}Sn_{0.06}, which is, however, beyond the scope of this study. Lin *et al.*³⁴ reported a linear relationship between the position of the Ge-Ge LO peak and the strain $E^{\parallel}$ and Sn composition x in the layer according to $\Delta\omega = \omega_{\text{GeSn}} - \omega_{\text{Ge}} = ax + bE^{\parallel}$ with $a = (-82 \pm 4) \text{ cm}^{-1}$ and $b = (-563 \pm 34) \text{ cm}^{-1}$. Using this relationship within the given precision³⁴ as well as the in-plane strain and Sn composition extracted from the RSM-XRD measurements (Table I), a peak shift between -0.45 cm^{-1} and $+0.48 \text{ cm}^{-1}$ is to be expected after this annealing step. The experimental value ($\Delta\omega \approx -0.5 \text{ cm}^{-1}$) falls within the predicted range. Yet, the uncertainty on parameters a and b (hence $\Delta\omega$) is rather high (5%–6%), and the peak shift expected in this system is very small due to the high compressive strain, rendering this analysis rather imprecise.

After 700 °C, less than half of the initial Sn content remains on substitutional lattice sites. The Sn surface concentration in the film (outside the precipitates) is likewise drastically reduced, while the precipitates are further enriched in Sn (27 at. % Sn). At these temperatures, simultaneous bulk in-diffusion is initiated, as revealed by SIMS (Figure 1(b)). Very different from the in-diffusion at lower temperatures, the resulting shape of the compositional profile (cf. SIMS profile in Figure 1(b)) shows an extended layer thickness (to $\sim 100 \text{ nm}$ from the surface) with a gradient Sn concentration, indicating a concentration dependent Sn

TABLE I. Summary of AES and RSM-XRD analysis of a 40 nm thin Ge_{0.94}Sn_{0.06} film as grown and after thermal annealing treatments. The Sn surface concentration is measured with scanning AES on the film surface and on the precipitates (Figure 4), respectively.

Temperature	Sn surface (at. %)	Sn island (at. %)	Sn substitutional (at. %)	$a^{\parallel} (\text{\AA})^a$	$a^{\perp} (\text{\AA})^b$	$R (\%)^c$	$E^{\parallel} (\%)^d$	$E^{\perp} (\%)^e$
	AES			RSM-XRD				
As grown	5.8	n/a	5.8 ± 0.1	5.658	5.742	0.4 ± 0.4	-0.85	0.62
500 °C	6.5 ± 0.6	n/a	5.7 ± 0.1	5.658	5.741	1.0 ± 0.4	-0.83	0.61
600 °C	5.4 ± 0.5	12.4 ± 1.6	5.2 ± 0.1	5.658	5.733	0.5 ± 0.4	-0.76	0.56
700 °C	3.8 ± 0.4	27.1 ± 4.9	2.5 ± 0.1	5.658	5.694	1.8 ± 0.4	-0.36	0.26
800 °C	<0.5	<0.5	0.5 ± 0.1	5.659	5.668	0.2 ± 0.4	-0.06	0.10

^a $a^{\parallel}$ is the in-plane lattice constant.

^b $a^{\perp}$ is the out-of-plane lattice constant.

^c R is the degree of relaxation.

^d $E^{\parallel}$ is the in-plane lattice strain.

^e $E^{\perp}$ is the out-of-plane lattice strain.

diffusion. Also, the ^{120}Sn signal intensity in the original 40 nm GeSn layer dropped by approximately 60%, in agreement with the large compositional changes detected by RSM-XRD (Table I). Yet, GIXRF measurements, which integrate over the precipitates and have an information depth of about 1 μm , denote that the total amount of Sn still present within the sample is comparable to the as grown case. This implies that no significant loss of Sn occurs due to thermal desorption processes. At very high temperatures (800 °C), the substitutional Sn content reaches the solubility limit, i.e., 0.5 at. % Sn,³ and the surface concentration (outside the precipitates) drops below the detection limit of the AES. This trend is consistent with a temperature-induced, diffusion-driven phase separation between Ge and Sn in the film and the preferable precipitation of Sn into large islands (see discussion below) rather than the growth of a Sn-rich overlayer as reported in Ref. 12. Note that in Ref. 12 rapid thermal annealing was used for thermal treatments, and hence, annealing times are much shorter (40 s) compared to our study (30 min), which might alter the strain relaxation mechanisms. With the strong reduction in Sn atoms incorporated in the Ge matrix, we expect significant changes in the molecular bonding structure as well, which is substantiated in a strong decrease in the Ge-Sn and Sn-Sn Raman signals on films annealed to 700 °C and 800 °C (Figure 2). In addition, the reduction in substitutional Sn content with increasing temperature is concurrent with a reduction in the out-of-plane lattice constant ($a^\perp$), while the in-plane lattice constant ($a^\parallel$) remains unchanged (Figure 3, Table I). The fixed in-plane lattice constant and, consequently, the negligible degree of relaxation ($<2\%$) denote that the layer remains strained and does not relax via the formation and propagation of misfit dislocation. This can directly be seen in the RSM-XRD maps (Figure 3), in which the (224) GeSn diffraction

peak remains aligned with the (224) Ge diffraction peak, i.e., on the pseudomorphic line. If the GeSn layer was to relax, the (224) GeSn peak would shift towards the relaxation line. Instead, with increasing temperature, this peak shifts gradually along the pseudomorphic line towards the Ge diffraction peak. After 800 °C annealing, the GeSn diffraction peak lies below the 2% Sn iso-compositional line. Thus, while the annealed film remains strained, i.e., the in-plane lattice constant of the layer ($a^\parallel_{\text{GeSn}}$) equals that of the substrate ($a^\parallel_{\text{Ge}}$), its absolute strain energy is reduced compared to the as grown layer as a consequence of the compositional changes (for $T \geq 500$ °C). In other words, the annealed GeSn film is more strain relaxed compared to the as grown layer since its Sn composition is lower and, consequently, the lattice mismatch between the Ge substrate and the GeSn film is reduced. With a 93% reduction in the in-plane compressive strain ($E^\parallel$) (Table I), the physical film properties such as band gap energy and charge carrier mobility will likewise be altered when compared to the initial (as grown) film properties.³⁷

B. Formation of surface structures: Islands and pits

A temperature induced phase separation and Sn precipitation in the form of *islands* is commonly observed for strained $\text{Ge}_{1-x}\text{Sn}_x$ films, irrespective of the Sn content, layer thickness, type of substrate, and growth process. The onset temperature for the Sn island formation has been reported to be around 150 °C,¹³ 450 °C,¹⁴ 500 °C,¹⁵ and 580 °C¹² for layers of 15 nm (5 at. % Sn), 30 nm (10 at. % Sn), 105 nm (8.5 at. % Sn), and 160 nm (8 at. % Sn) thicknesses, respectively. In our study, the formation temperature of the Sn islands was found between 400 °C and 500 °C, for both a thin (40 nm) and a thick (75 nm) GeSn layer (6 at. % Sn). Remarkably, no significant changes were detected in the (substitutional) Sn content and Sn distribution (Table I, Figure 1), in the layer strain or even in the molecular configuration (Figure 2) in this temperature range. This supports the recent findings¹⁸ which showed that, contrary to the common belief, the Sn-cluster formation is not the main driving force for strain relaxation in the CVD-grown $\text{Ge}_{0.93}\text{Sn}_{0.07}$ layers but solely a phenomenon occurring at the same time, governed by the thermodynamic solubility limit of Sn in Ge. The decoupling between strain relaxation and Sn-precipitation was also verified in Ref. 38. In this study, relaxation was induced by an increasing layer thickness rather than by thermal treatments, and in these cases (where ultimately 100% relaxation occurs), the EXAFS data showed no significant change in the local atomic ordering of the Sn atoms, and formation of Sn dimers or clusters remains below 2.5% of the total Sn atoms in CVD-grown $\text{Ge}_{1-x}\text{Sn}_x$ films ($0.06 \leq x \leq 0.124$). As evident from AFM and SEM images (Figure 4), the islands do not only decorate the film surface but also penetrate through the (complete) GeSn layer and are typically located in a cavity. Similarities to the β -Sn wires formed on MBE-grown $\text{Ge}_{0.83}\text{Sn}_{0.17}$ films after thermal annealing might be drawn, which were also found to be embedded and to extend to the GeSn/Ge interface.¹⁷ Two separated phases are clearly distinguishable in the near

FIG. 2. Raman measurements (633 nm He-Ne laser excitation source) of 40 nm $\text{Ge}_{0.94}\text{Sn}_{0.06}$ films as grown and after different annealing treatments. A bulk Ge(100) wafer (dashed line) was measured as reference (Ge-Ge phonon mode at 300 cm^{-1}). The inset shows a close-up view of the Sn-Sn like ($\sim 184 \text{ cm}^{-1}$) and Ge-Sn ($\sim 262 \text{ cm}^{-1}$) vibrational modes. A more detailed discussion on the assignment of the phonon modes can be found in the text.

FIG. 3. RSM-XRD measurements of a 40 nm thin $\text{Ge}_{0.94}\text{Sn}_{0.06}$ film (a) as grown and after 500 °C (b), 700 °C (c), and 800 °C (d) annealing. The pseudomorphic line, the relaxation line, as well as the iso-compositional lines for 0%, 2%, 4%, and 6% Sn composition are shown as black solid lines.

surface region of the islands (Figures 5(a)–5(c)) using near-field microscopy (i.e., two distinct optical absorption regions), akin to the observation made by Fournier-Lupien¹⁶ on thermally treated $\text{Ge}_{0.88}\text{Sn}_{0.12}$ films grown by CVD. We presumably assign these phases to pure Sn as well as Ge and/or GeSn close to the solubility limit (1 at. % Sn). Note that for an IR-SNOM image recorded at $\lambda = 5.4 \mu\text{m}$, the areas with a high Sn content should exhibit a higher IR signal amplitude due to the larger refractive index³⁹ of Sn ($n_{\text{Sn}} = 9.5$ ⁴⁰) compared to pure Ge ($n_{\text{Ge}} = 4.0$ ⁴¹) at this wavelength. Since there is no one-to-one correspondence between topography and infrared signal, a topography induced image

contrast can be excluded. In the area around the pattern, where a lower segregation grade of the two materials is expected, the IR signal amplitude lies between that observed in regions with higher (light areas) and lower Sn (dark areas) content.

The work of Deng *et al.*¹³ depicts a similar characteristic of the islands, with two separated phases, i.e., pure Sn and Ge(Sn). However, in their study, Sn islands were observed already before the thermal treatment on the as grown layer, which may alter their formation mechanisms due to the continuous supply of Ge and Sn atoms from the vapor phase during MBE deposition. Chen *et al.*¹⁴ likewise postulated that the islands formed after annealing are composed of a mixed-phase, i.e., Ge, $\text{Ge}_{0.99}\text{Sn}_{0.01}$, and β -Sn, and are Sn enriched at the surface. Whereas the latter argument was validated by AES measurements, the former hypothesis could not be proven experimentally in their study on CVD-grown $\text{Ge}_{0.9}\text{Sn}_{0.1}$ films.

With increasing annealing temperature ($500^\circ\text{C} \leq T < 800^\circ\text{C}$), the apparent height and circumference of the islands increase, while the islands retain their shape, i.e., dome and non-spherical droplet structure. Whether Ostwald ripening (coarsening of particle size distribution) of these 2-phase particles is a relevant process at these temperature/annealing times cannot be clearly identified. Due to the large inter-island distance ($>5 \mu\text{m}$), a reliable size distribution could not be measured with AFM. Optical microscopy images, however, must be interpreted with care as both islands and holes will give rise to light scattering, and therefore, appear both as bright spots in the microscopy image. The large-area SEM images (data not shown) show a slight decrease in particle density along with a simultaneous increase in particle size between 600 °C and 700 °C, suggesting an Ostwald ripening process. Yet, due to the low contrast, the islands are difficult to distinguish from holes and

FIG. 4. AFM topography (a), (b), (e), and SEM (c) images recorded on a 40 nm $\text{Ge}_{0.94}\text{Sn}_{0.06}$ film after 600 °C (a) and 700 °C (b)–(e) anneal. (d) Height profile taken along the line indicated by arrows in (b). (e) 3D representation ($z = 180 \text{ nm}$) of the area indicated by the arrows in (b).

FIG. 5. AFM, IR-SNOM, and SEM measurements of a 40 nm $\text{Ge}_{0.94}\text{Sn}_{0.06}$ film after 700 °C (a)–(c) and 800 °C (d)–(f) anneal. (a), (d) and (c), (f) represent the surface topography measured by AFM and SEM, respectively. (b), (e) The near-field infrared signal (4th harmonic) recorded at a wavelength of 5.4 μm , whereas the bright regions exhibit the highest IR signal amplitude and the dark regions exhibit the lowest IR signal amplitude.

other artifacts, rendering the particle density and size distribution analysis challenging and rather unreliable. Beyond 800 °C, a large fraction of the islands evaporates from the surface (Figures 5(d)–5(f)). In agreement to this, GIXRF measurements of a 40 nm GeSn film with initial 5 at. % Sn (data not shown) verify a 24% reduction in the total Sn content after annealing to 800 °C. Note that the information depth in this GIXRF measurement (at 5 keV) amounts to $\sim 1 \mu\text{m}$, hence this technique will also detect the Sn that is diffused deep into the bulk material (cf. Figure 1(b)). Interestingly, the majority of the remaining cavities exhibit a smaller dimension (200–500 nm) compared to the dimension of the initial islands (500–1000 nm). The residual material in the cavity and the crater rim seems to be enriched in Sn compared to the surrounding GeSn layer, which exhibits a Sn concentration close to the solubility limit of Sn in Ge (0.5 at. % Sn) (Table I).

Despite the Sn-enriched islands, we also observed squared surface depressions or *pits* of much smaller dimensions, randomly distributed over the annealed film surface (Figures 4 and 6). In some instances, these features are located within the cavity of a Sn-enriched island (Figure 4(c), white circles). The formation temperature of the pits is comparable to that of the islands, i.e., between 400 °C and 500 °C. While a small increase in the rms surface roughness can be discerned at this temperature (Figure 6(g)), the film properties remain unchanged on the atomic level such as the molecular configuration (Figure 2) or the amount and distribution of Sn in the layer (Figure 1, Table I), as highlighted in the above discussion. The pits are not formed by cooperative nucleation adjacent to an island,^{13,42} and the absence of agglomerated material at the pit rim implies no major diffusional mass transport from the center to the outer edges.¹⁴ Their squared shape and faceting close to the {111} and {113} crystallographic planes (Figure 7) may suggest analogies to etch pits revealed by chemical (defect) etching, in which the material is preferentially removed in the strain field around dislocations.^{4,43} Yet, defects as root cause of

these pits can be ruled out as no misfit or threading dislocations were observed in the pit vicinity in cross-sectional TEM images of the 40 nm film (Figure 7). Also, no particulates or impurity precipitates^{13,44} were discerned at the hetero-interface. With increasing annealing temperature (500 °C $\leq T < 800$ °C), the pits seem to coalesce as their density decreases under invariant surface coverage and total pit volume (Figure 6). The pits do not penetrate to the hetero-interface even at high annealing temperatures. After 800 °C annealing, (Figure 6(e)) pits are absent, implying atomic diffusional processes might replenish the pits. The large remaining cavities/holes still visible on the AFM image after 800 °C annealing (Figure 6(e)) originate from the Sn-rich islands (discussion above) and should not be confused with the pits, which are of much smaller dimensions.

Reports on surface pits on thermally treated, strained $\text{Ge}_{1-x}\text{Sn}_x$ films are very scarce. Takeuchi *et al.*⁹ observed shallow and deep pits of comparable dimensions on a 220 nm (2.7 at. % Sn) MBE-grown film annealed to 600 °C. Yet, in their study, misfit dislocations were found at the Ge substrate interface, and the pits were correlated to (long wavelength) undulation on the surface (cross-hatch pattern). Neither of these characteristics are in-line with our observations on the 40 nm GeSn film, in which the pits were formed in a defect-less and very smooth layer (Figure 7(c)). We have observed, however, similar surface pits on a 75 nm $\text{Ge}_{0.94}\text{Sn}_{0.06}$ film, which exhibits a cross-hatch morphology (prior to annealing) such as reported in Ref. 9. The 75 nm film exceeds the critical thickness for plastic strain relaxation, which explains the observation of a cross-hatch pattern on the surface of the as grown film. In contrast, the thin film (40 nm) is fully strained after film growth, as can be inferred from the RSM-XRD (Table I). This is in agreement with Ref. 45 where it was reported that metastable films, i.e., films grown under low-temperature conditions, may reach higher critical thickness values than those predicted by the Matthews and Blakeslee⁴⁶ and Frank and van der Merwe⁴⁷ equilibrium models as under these growth conditions kinetic

FIG. 6. (a)–(e) AFM topography images of 40 nm $\text{Ge}_{0.94}\text{Sn}_{0.06}$ films after deposition (a) and after annealing to 500 °C (b), 600 °C (c), 700 °C (d), as well as 800 °C (e). (f) A reference layer (1.1%Sn) after 700 °C annealing. (g)–(i) Statistical analysis of the AFM images shown in (a)–(e). (g) rms roughness extracted from $(1 \times 1) \mu\text{m}^2$ and $(5 \times 5) \mu\text{m}^2$ scan areas. The Sn-enriched clusters (see Figure 4) are included in the roughness analysis of the $(5 \times 5) \mu\text{m}^2$ images. (h) Pit density determined by flooding analysis from a $(1 \times 1) \mu\text{m}^2$ scan area with a minimum feature size of 3 nm (closed circles) or 5 nm (open square). (i) Projected surface area of the surface pits (left axis) and total pit size (right axis) given in fraction of Ge monolayer (ML) with 1 ML = 6.24×10^{14} Ge atoms/cm² and 4.2×10^{22} Ge atoms/cm³. Volume analysis was performed on $(1 \times 1) \mu\text{m}^2$ images.

barriers are likely to delay the onset of misfit dislocation formation and/or motion.⁴⁵

It has been argued before^{42,48} that thermally activated surface roughening (stress-driven surface diffusion) may take the form of pits, yielding partial strain relief in the film through purely elastic deformation. These pits, in turn, provide a source for low-barrier nucleation of dislocations, which finally releases the strain in the layer. In other words,

the surface may roughen (form pits) *before* any dislocations are formed.⁴⁸ This may explain why no defects are observed in the pit vicinity of the thin film system (Figure 7). As phase separation is a competing mechanism for strain release in this system, the rate for dislocation nucleation may effectively be reduced. After strain relief (independent on the mechanism), the surface gradually smoothens to lower its energy,⁴⁸ justifying the absence of pits after annealing to

FIG. 7. Cross-sectional TEM images of a 40 nm $\text{Ge}_{0.94}\text{Sn}_{0.06}$ film annealed to 500 °C, showing the faceting and typical dimensions of a single pit (a) as well as two overlapping pits (b). (c) On a large-scale, the surface is smooth without any long-wavelength surface undulations.

800 °C. We have no direct experimental evidence whether the pits observed in our study provide a means of local strain release in the thin layer as the pits cover less than 3% of the surface (Figure 6(i)), rendering any pit induced changes in lattice strain non-measurable (below detection limit). In addition, with increasing annealing temperature, pit formation and phase separation occur simultaneously in the layer so that no clear distinction can be made either. Yet, based on the following observations, we anticipate that the pit formation may be primarily attributed to local strain release: (1) The absence of pits (or the replenishment of pits) after 800 °C annealing (Figure 6(e)), after which both the Sn content, and consequently, the strain in the layer are decreased accordingly (Table I, Figure 1), ceasing this type of surface roughening. (2) No pits are observed on an annealed, diluted (1 at. % Sn) 40 nm reference layer (Figure 6(f)).

We speculate that the pits observed on the thin and the thick layer systems (as well as in Ref. 9) have the same origin, i.e., stress-driven surface diffusion⁴⁸ and are not the consequence of misfit dislocations. On the contrary, if the system exhibits a high defect density before annealing, as is the case for the thick GeSn layer or the system studied in Ref. 9, these pits may rather catalyze the formation and propagation of dislocations⁴⁸ and hence strain relaxation by misfit dislocation in the GeSn film.

It should be noted that surface pits faceted into low energy planes {113} have also been found to result from

diffusional and desorption processes in thermally annealed, relaxed $\text{Si}_{0.8}\text{Ge}_{0.2}$ films.⁴⁹ In our study, *in-situ* AES analysis after thermal treatments (data not shown) confirms that the temperature of pit formation and surface oxide desorption are identical, suggesting thermal etching and preferential oxide desorption as another origin of the pits. Yet, as the pit volume (Figure 6(i)) accounts for only a fraction of a monolayer (ML), we expect this mechanism to be of minor importance only.

C. Self-assembly of surface structures: Circular patterns and trenches

Another intriguing phenomenon observed on the annealed $\text{Ge}_{0.94}\text{Sn}_{0.06}$ layers is the self-assembly of the above mentioned surface features. Under certain circumstances, the Sn-rich islands tend to self-assemble into a circular pattern centered around a large particle (Figure 8) or result into a random network of trenches (Figure 9). Remarkably, these self-organized patterns are scattered over the sample surface, and the circular patterns were only observed on the thin films (40 nm), whereas the trenches could be only seen on the thick film (75 nm) system.

The self-organization of the Sn-rich islands into a circular pattern (Figure 8(a)) is comparable to the pattern observed on thin Au-Si alloys.⁵⁰ Venkatachalam *et al.*⁵⁰ ascribed this phenomenon to result from a two-dimensional compositional banding of the liquid alloy during epitaxial re-crystallization. These authors compare this initial phase separation with the lamellae-like growth (eutectic structure) observed in bulk eutectic phases. The compositional banding is believed⁵⁰ to be initiated by a nucleation event such as a large particle that eventually perturbs the local in-plane alloy distribution. After pattern formation, the region around the centered particle is more strongly depleted from the solute than the region surrounding the smaller particles in the ring structure.⁵⁰ A closer look to the microscopy image in Figure 8(a) reveals different circular regions (labeled A–D) around this center particle. The diameter of zones B, C, and D amounts to 73 μm , 130 μm , and 228 μm , respectively. In contrast to zones A, B, and D, zone C contains a very limited number of particles and is almost featureless. AFM measurements (Figure 8(b)) reveal that the surface morphology significantly varies between these zones, i.e., some of the bright spots visible in the microscopy image correspond to squared surface depressions or pits, such as reported above, rather than to islands. The pit density is highest in zone A, which accommodates no islands, and decreases with increasing distance from the center particle. Further away from the center (zone D), the pit density is increased again and comparable to the remaining surface (far away from the large particle). This distinctive morphological evolution substantiates the argument of compositional fluctuations around the center particle stated in Ref. 50, assuming that the formation mechanism of these pits is attributed to the film composition and hence the strain in the layer (see discussion above). The strain field associated with the large particle causes a locally enhanced strain in zone A, which is released by the formation of pits. As this region is highly likely to be strongly depleted in Sn (diffusional transfer to the central particle⁵⁰),

FIG. 8. Optical microscopy (a) and AFM measurements (b) at the respective regions as indicated by the labels A–D of a 40 nm $\text{Ge}_{0.94}\text{Sn}_{0.06}$ film annealed above 700 °C. The self-organization of islands/pits into circular pattern around a large center particle is clearly visible.

Sn-island formation is not initiated. This finding further supports our hypothesis stated above, in which we attributed the pits to local strain release. Further away from the center, i.e., in zone C, the strain field is reduced due to the large distance from the center particle and due to the Sn-deficiency in this region.⁵⁰ Consequently, neither pits nor islands will be formed in this region, similar to the morphological stability observed on the diluted (1 at. %) GeSn reference sample. Zone D exhibits a Sn concentration which is comparable to

the remainder of the film. In this region, the high Sn content in the layer and the strain associated with this will lead to island and pit formation as discussed above.

The second self-assembled pattern we have observed in this study is the formation of a random network of trenches (Figure 9), comparable to the pattern reported in Refs. 13, 14, and 16 for MBE- and CVD-grown films, respectively. In agreement with Ref. 13, the total length of each trench differs, while its width is typically around 150 nm. The trenches

FIG. 9. Optical microscopy (a), Sn AES map (b), AFM topography (c), and phase image (d) of the region indicated with the white square in (c) of a 75 nm $\text{Ge}_{0.94}\text{Sn}_{0.06}$ film annealed to 450 °C.

run along preferred crystallographic directions and form a connection between a small and a large island, the latter being enriched in Sn (on the surface) relative to its surrounding, as verified by AES measurements (Figure 9(b)). The density of these trenches varies laterally over the surface, i.e., regions with a high trench density (center) adjoined regions that exhibit only large islands, but no trenches (Figure 9(a)). This suggests that the formation of these trenches may be linked to temperature, composition, and/or strain in the film, as these parameters may vary over the film surface. Deng *et al.*¹³ suggested that the “trench-free” regions mark the initial stage of the trench formation process, which is described by the formation of a Sn island (1). In a subsequent step (2), Ge trapped in this island will agglomerate and precipitate from this island, followed by the migration of the Sn island over the surface and the formation of a trench (3). In the study of Fournier-Lupien,¹⁶ this phenomenon took place on time scales much shorter than 1 s. These authors also observed mass transport between neighboring islands and a subtle material exchange between the trenches and neighboring terraces, where Sn diffuses away from the trenches and wets the terraces.¹⁶ Although we have observed the precipitation of islands containing two distinct phases on both the thick and the thin film systems, consistent with stages 1 and 2 described in Ref. 13, migration of these islands and trench formation was not favored on the thin film system even at very high annealing temperatures. Deng *et al.* postulated that the presence of epitaxial strain in the layer would impact the kinetic pathway of the phase separation, yielding these randomly oriented micro-trenches. However, the strain in the thin film system is expected to be higher than in the thick film system, as the latter showed signs of strain relaxation prior to annealing (cross-hatch pattern). It was shown in a recent study¹⁷ that the film thickness can be critical to the morphological evolution in the MBE-grown $\text{Ge}_{0.83}\text{Sn}_{0.017}$ films. These authors reported the thermally activated (by rapid thermal annealing) formation of β -Sn wires, through a mechanism akin to cellular precipitation, which was only observed on the films with a thickness equal to or above 25 nm. Being mediated by grain boundary diffusion, this process appears to be favored in thick films where Sn precipitation already occurs at low temperatures ($\sim 280^\circ\text{C}$).¹⁷ In contrast, in thin films, Sn segregation and precipitation happen at higher temperatures only ($>350^\circ\text{C}$), where bulk diffusion and hence direct growth of Sn islands seem to be more likely. In our study, however, the temperature to initiate Sn precipitation is similar for both the thick and the thin films (400°C – 500°C). It remains speculative why the island migration is inhibited in the thin film system in our study, considering the fact that the type of substrate, Sn content, and film thickness as well as the growth method are comparable to those in Ref. 13. This suggests that other parameters than epitaxial strain (e.g., defect density, surface/interface cleanliness, etc.) may play a critical role too. One could contemplate that misfit dislocation at the hetero-interface may drive the island migration and hence trench formation, as the as grown thick film exhibits a higher defect density. As the defect density was not reported in Refs. 13 and 14, no further conclusion can be drawn here.

IV. CONCLUSION

Our results demonstrate that relaxation via dislocation formation and propagation is not an intrinsic phenomenon to MBE-grown, compressively strained $\text{Ge}_{0.94}\text{Sn}_{0.06}$ films investigated in this study. Under certain conditions and/or film properties, both diffusion-driven phase separation and morphological changes such as Sn island and pit formation appear to be the dominant mechanisms for energy reduction in these films. Importantly, these morphological surface instabilities are not necessarily reflected in compositional or strain measurements such as XRD. Yet, they should not be ignored as they deteriorate film properties such as surface roughness, defect density, etc., which is highly undesirable for further processing steps and impairs with the integration of these films in advanced devices. It remains, however, speculative whether the interfacial properties prior to annealing such as defect density, interfacial cleanliness, etc., play a key role in determining the dominant pathway for strain relaxation. The $\text{Ge}_{0.94}\text{Sn}_{0.06}$ films are found to be thermally stable up to approximately 400°C , with no measurable changes in strain, substitutional Sn content, molecular configuration, or surface morphology. As our data indicate, the thermal stability of these films appears to be governed by compositional instabilities, which are intrinsic to alloys with concentrations above the solubility limit.

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¹J. D. Sau and M. L. Cohen, “Possibility of increased mobility in Ge-Sn alloy system,” *Phys. Rev. B* **75**, 045208 (2007).

²P. Moontragoon, Z. Ikonik, and P. Harrison, “Band structure calculations of Si-Ge-Sn alloys: Achieving direct band gap materials,” *Semicond. Sci. Technol.* **22**(7), 742–748 (2007).

³R. W. Olesinski and G. J. Abbaschian, “The Ge-Sn (germanium-tin) system,” *Bull. Alloy Phase Diagrams* **5**(3), 265–271 (1984).

⁴F. Gencarelli, B. Vincent, L. Souriau, O. Richard, W. Vandervorst, R. Loo, M. Caymax, and M. Heyns, “Low-temperature Ge and GeSn chemical vapor deposition using Ge_2H_6 ,” *Thin Solid Films* **520**(8), 3211–3215 (2012).

⁵B. Vincent, F. Gencarelli, H. Bender, C. Merckling, B. Douhard, D. H. Petersen, O. Hansen, H. H. Henrichsen, J. Meersschant, W. Vandervorst, M. Heyns, R. Loo, and M. Caymax, “Undoped and *in-situ* B doped GeSn epitaxial growth on Ge by atmospheric pressure-chemical vapor deposition,” *Appl. Phys. Lett.* **99**, 152103 (2011).

⁶L. Jiang, C. Xu, J. D. Gallagher, R. Favaro, T. Aoki, J. Menendez, and J. Kouvetakis, “Development of light emitting group IV ternary alloys on Si platforms for long wavelength optoelectronic applications,” *Chem. Mater.* **26**(8), 2522–2531 (2014).

⁷S. Su, W. Wang, B. Cheng, G. Zhang, W. Hu, C. Xue, Y. Zuo, and Q. Wang, “Epitaxial growth and thermal stability of $\text{Ge}_{1-x}\text{Sn}_x$ alloys on Ge-buffered Si(001) substrates,” *J. Cryst. Growth* **317**(1), 43–46 (2011).

- ⁸I. S. Yu, T. H. Wu, K. Y. Wu, H. H. Cheng, V. I. Mashanov, A. I. Nikiiforov, O. P. Pchelyakov, and X. S. Wu, "Investigation of $\text{Ge}_{1-x}\text{Sn}_x/\text{Ge}$ with high Sn composition grown at low-temperature," *AIP Adv.* **1**, 042118 (2011).
- ⁹S. Takeuchi, A. Sakai, K. Yamamoto, O. Nakatsuka, M. Ogawa, and S. Zaima, "Growth and structure evaluation of strain-relaxed $\text{Ge}_{1-x}\text{Sn}_x$ buffer layers grown on various types of substrates," *Semicond. Sci. Technol.* **22**, S231 (2007).
- ¹⁰S. Takeuchi, A. Sakai, O. Nakatsuka, M. Ogawa, and S. Zaima, "Tensile strained Ge layers on strain-relaxed $\text{Ge}_{1-x}\text{Sn}_x$ /virtual Ge substrates," *Thin Solid Films* **517**(1), 159–162 (2008).
- ¹¹S. Zaima, O. Nakatsuka, N. Taoka, M. Kurosawa, W. Takeuchi, and M. Sakashita, "Growth and applications of GeSn-related group-IV semiconductor materials," *Sci. Technol. Adv. Mater.* **16**(4), 043502 (2015).
- ¹²H. Li, Y. X. Cui, K. Y. Wu, W. K. Tseng, H. H. Cheng, and H. Chen, "Strain relaxation and Sn segregation in GeSn epilayers under thermal treatment," *Appl. Phys. Lett.* **102**, 251907 (2013).
- ¹³X. Deng, B.-K. Yang, S. A. Hackney, M. Krishnamurthy, and D. R. M. Williams, "Formation of self-assembled quantum wires during epitaxial growth of strained GeSn alloys on Ge(100): Trench excavation by migrating Sn islands," *Phys. Rev. Lett.* **80**(5), 1022–1025 (1998).
- ¹⁴R. Chen, Y.-C. Huang, S. Gupta, A. C. Lin, E. Sanchez, Y. Kim, K. C. Saraswat, T. I. Kamins, and J. S. Harris, "Material characterization of high Sn-content, compressively-strained GeSn epitaxial films after rapid thermal processing," *J. Cryst. Growth* **365**, 29–34 (2013).
- ¹⁵W. Wang, L. Li, Q. Zhou, J. Pan, Z. Zhang, E. S. Tok, and Y.-C. Yeo, "Tin surface segregation, desorption, and island formation during post-growth annealing of strained epitaxial $\text{Ge}_{1-x}\text{Sn}_x$ layer on Ge(0 0 1) substrate," *Appl. Surf. Sci.* **321**, 240–244 (2014).
- ¹⁶J.-H. Fournier-Lupien, D. Chagnon, P. Lévesque, A. A. AlMutairi, S. Wirths, E. Pippel, G. Mussler, J.-M. Hartmann, S. Mantl, D. Buca, and O. Moutanabbir, "In situ studies of germanium-tin and silicon-germanium-tin thermal stability," *ECS Trans.* **64**(6), 903–911 (2014).
- ¹⁷W. Wang, L. Li, E. S. Tok, and Y.-C. Yeo, "Self-assembly of tin wires via phase transformation of heteroepitaxial germanium-tin on germanium substrate," *J. Appl. Phys.* **117**(22), 225304 (2015).
- ¹⁸A. Kumar, J. Demeulemeester, J. Bogdanowicz, J. Bran, D. Melkonyan, C. Fleischmann, F. Gencarelli, Y. Shimura, W. Wang, R. Loo, and W. Vandervorst, "On the interplay between relaxation, defect formation, and atomic Sn distribution in $\text{Ge}(1-x)\text{Sn}(x)$ unraveled with atom probe tomography," *J. Appl. Phys.* **118**, 025302 (2015).
- ¹⁹A. T. Fiory, J. C. Bean, R. Hull, and S. Nakahara, "Thermal relaxation of metastable strained-layer $\text{Ge}_x\text{Si}_{1-x}/\text{Si}$ epitaxy," *Phys. Rev. B* **31**, 4063–4065 (1985).
- ²⁰S. Gupta, X. Gong, R. Zhang, Y.-C. Yeo, S. Takagi, and K. C. Saraswat, "New materials for post-Si computing: Ge and GeSn devices," *MRS Bull.* **39**(8), 678–686 (2014).
- ²¹S. Takeuchi, Y. Shimura, T. Nishimura, B. Vincent, G. Eneman, T. Clarysse, J. Demeulemeester, A. Vantomme, J. Dekoster, M. Caymax, R. Loo, A. Sakai, O. Nakatsuka, and S. Zaima, " $\text{Ge}_{1-x}\text{Sn}_x$ stressors for strained-Ge CMOS," *Solid-State Electron.* **60**, 53–57 (2011).
- ²²Y. Shimura, N. Tsutsui, O. Nakatsuka, A. Sakai, and S. Zaima, "Low temperature growth of $\text{Ge}_{1-x}\text{Sn}_x$ buffer layers for tensile-strained Ge layers," *Thin Solid Films* **518**(6), S2–S5 (2010).
- ²³J. Lubeck, B. Beckhoff, R. Fliegau, I. Holfelder, P. Hoenicke, M. Mueller, B. Pollakowski, F. Reinhardt, and J. Weser, "A novel instrument for quantitative nanoanalytics involving complementary X-ray methodologies," *Rev. Sci. Instrum.* **84**, 045106 (2013).
- ²⁴B. Beckhoff, "Reference-free X-ray spectrometry based on metrology using synchrotron radiation," *J. Anal. At. Spectrom.* **23**, 845–853 (2008).
- ²⁵M. Müller, P. Hönicke, B. Detlefs, and C. Fleischmann, "Characterization of high-k nanolayers by grazing incidence X-ray spectrometry," *Materials* **7**(4), 3147–3159 (2014).
- ²⁶R. R. Lieten, J. W. Seo, S. Decoster, A. Vantomme, S. Peters, K. C. Bustillo, E. E. Haller, M. Menghini, and J.-P. Locquet, "Tensile strained GeSn on Si by solid phase epitaxy," *Appl. Phys. Lett.* **102**, 052106 (2013).
- ²⁷H. J. McSkimin and P. Andreatch, "Elastic moduli of germanium versus hydrostatic pressure at 25.0°C and at –195.8°C," *J. Appl. Phys.* **34**(3), 651–655 (1963).
- ²⁸S.-G. Shen, "Calculation of the elastic properties of semiconductors," *J. Phys.: Condens. Matter* **6**(42), 8733–8743 (1994).
- ²⁹I. Horcas, R. Fernandez, J. M. Gomez-Rodriguez, J. Colchero, J. Gomez-Herrero, and A. M. Baro, "WSXM: A software for scanning probe microscopy and a tool for nanotechnology," *Rev. Sci. Instrum.* **78**, 013705 (2007).
- ³⁰P. Hermann, A. Hoehl, P. Patoka, F. Huth, E. Rühl, and G. Ulm, "Near-field imaging and nano-Fourier-transform infrared spectroscopy using broadband synchrotron radiation," *Opt. Express* **21**, 2913–2919 (2013).
- ³¹P. Hermann, A. Hoehl, G. Ulrich, C. Fleischmann, A. Hermelink, B. Kästner, P. Patoka, A. Hornemann, B. Beckhoff, E. Rühl, and G. Ulm, "Characterization of semiconductor materials using synchrotron radiation-based near-field infrared microscopy and nano-FTIR spectroscopy," *Opt. Express* **22**(15), 17948–17958 (2014).
- ³²A. J. Huber, A. Ziegler, T. Köck, and R. Hillenbrand, "Infrared nanoscopy of strained semiconductors," *Nat. Nanotechnol.* **4**(153), 153–157 (2009).
- ³³V. D'Costa, J. Tolle, R. Roucka, C. Poweleit, J. Kouvetakis, and J. Menendez, "Raman scattering in $\text{Ge}_{1-y}\text{Sn}_y$ alloys," *Solid State Commun.* **144**, 240–244 (2007).
- ³⁴H. Lin, R. Chen, Y. Huo, T. I. Kamins, and J. S. Harris, "Raman study of strained $\text{Ge}_{1-x}\text{Sn}_x$ alloys," *Appl. Phys. Lett.* **98**, 261917 (2011).
- ³⁵M. Rojas-Lopez, H. Navarro-Contreras, P. Desjardins, O. Gurdal, N. Taylor, J. R. A. Carlsson, and J. E. Greene, "Raman scattering from fully strained $\text{Ge}_{1-x}\text{Sn}_x$ ($x < 0.22$) alloys grown on Ge(001)2X1 by low-temperature molecular beam epitaxy," *J. Appl. Phys.* **84**(4), 2219–2223 (1998).
- ³⁶I. D. Wolf, J. Jiménez, J.-P. Landesman, C. Frigeri, P. Braun, E. D. Silva, and E. Calvet, *Raman and Luminescence Spectroscopy for Microelectronics: Catalogue of Optical and Physical Parameters "Nostradamus" Project SMT4-CT-95-2024* (European Commission, 1998), ISBN: 92-828-5011-1.
- ³⁷O. Nakatsuka, Y. Shimura, W. Takeuchi, N. Taoka, and S. Zaima, "Development of epitaxial growth technology for $\text{Ge}_{1-x}\text{Sn}_x$ alloy and study of its properties for Ge nanoelectronics," *Solid-State Electron.* **83**, 82–86 (2013).
- ³⁸F. Gencarelli, D. Grandjean, Y. Shimura, B. Vincent, D. Banerjee, A. Vantomme, W. Vandervorst, R. Loo, M. Heyns, and K. Temst, "Extended X-ray absorption fine structure investigation of Sn local environment in strained and relaxed CVD grown epitaxial $\text{Ge}_{1-x}\text{Sn}_x$ films," *J. Appl. Phys.* **117**, 095702 (2015).
- ³⁹F. Huth, M. Schnell, J. Wittborn, N. Ocelic, and R. Hillenbrand, "Infrared-spectroscopic nanoimaging with a thermal source," *Nat. Mater.* **10**, 352–356 (2011).
- ⁴⁰A. I. Golovashkin and G. P. Motulevich, "Optical and electrical properties of tin," *Sov. Phys. JETP* **19**(2), 310–317 (1964).
- ⁴¹H. W. Icenogle, B. C. Platt, and W. L. Wolfe, "Refractive indexes and temperature coefficients of germanium and silicon," *Appl. Opt.* **15**(10), 2348–2351 (1976).
- ⁴²D. E. Jesson, K. M. Chen, S. J. Pennycook, T. Thundat, and R. J. Warmack, "Morphological evolution of strained films by cooperative nucleation," *Phys. Rev. Lett.* **77**, 1330–1333 (1996).
- ⁴³C. Claeys and E. Simon, *Fundamental and Technological Aspects of Extended Defects in Germanium*, Materials Science, edited by R. Hull, J. R. M. Osgood, and J. P. H. Warlimont (Springer, 2009).
- ⁴⁴J. D. Weil, X. Deng, and M. Krishnamurthy, "Preferential nucleation of Ge islands at self-organized pits formed during the growth of thin Si buffer layers on Si(110)," *J. Appl. Phys.* **83**(1), 212–216 (1998).
- ⁴⁵F. Gencarelli, B. Vincent, J. Demeulemeester, A. Vantomme, A. Moussa, A. Franquet, A. Kumar, H. Bender, J. Meersschaet, W. Vandervorst, R. Loo, M. Caymax, K. Temst, and M. Heyns, "Crystalline properties and strain relaxation mechanism of CVD grown GeSn," *ECS J. Solid State Sci. Technol.* **2**(4), P134–P137 (2013).
- ⁴⁶J. W. Matthews and A. E. Blakeslee, "Defects in epitaxial multilayers: I. Misfit dislocations," *J. Cryst. Growth* **27**(118), 118–125 (1974).
- ⁴⁷F. C. Frank and J. H. van der Merwe, "One-dimensional dislocations. I. Static theory," *Proc. R. Soc. London, Ser. A* **198**(1053), 205–216 (1949).
- ⁴⁸J. Tersoff and F. K. LeGoues, "Competing relaxation mechanisms in strained layers," *Phys. Rev. Lett.* **72**, 3570–3573 (1994).
- ⁴⁹Z. Zhang, J. S. Pan, J. Zhang, and E. S. Tok, "Kinetics of Ge diffusion, desorption and pit formation dynamics during annealing of $\text{Si}_{0.8}\text{Ge}_{0.2}/\text{Si}$ (001) virtual substrates," *Phys. Chem. Chem. Phys.* **12**, 7171–7183 (2010).
- ⁵⁰D. K. Venkatachalam, N. H. Fletcher, D. K. Sood, and R. G. Elliman, "Self-assembled nanoparticle spirals from two-dimensional compositional banding in thin films," *Appl. Phys. Lett.* **94**, 213110 (2009).