Interplay between relaxation and Sn segregation during thermal annealing of GeSn strained layers

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Interplay between relaxation and Sn segregation during thermal annealing of GeSn strained layers

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The effect of thermal annealing on epitaxial GeSn (6.5% Sn) strained layers grown on Ge-buffered Si(100) wafers has been investigated using Rutherford backscattering spectrometry and X-ray diffraction to unambiguously determine the Sn substitutional content as well as the elastic strain in the layers. Vacuum annealing at temperatures below 400 °C for 20 min has no noticeable effect on the strain in the epitaxial layers. Once the temperature was raised above 400 °C, however, relaxation of the layer sets in and the GeSn layer has essentially completely relaxed following a 20 min anneal at 650 °C. Using Rutherford backscattering and channelling spectrometry to provide compositional information as a function of depth enables one to monitor the effect of the thermal anneal on the Sn distribution throughout the layer, and also to *directly* extract their substitutional fraction (i.e., their solubility in the lattice). The results obtained show that when the relaxation initially sets in both the Ge and the Sn remain firmly bound in substitutional lattice sites and it is only around 600 °C, and after substantial relaxation has taken place, that Sn is finally expelled from lattice sites and diffuses to the surface of the sample. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4964692>]

INTRODUCTION

With it becoming increasingly difficult to achieve the continuous scaling of microelectronic devices, attention has now begun to turn to finding alternative materials to silicon. Were silicon to be replaced by germanium, then strained $\text{Ge}_{1-x}\text{Sn}_x$ could perform a similar role to that played by strained $\text{Si}_{1-y}\text{Ge}_y$ in silicon-based devices.¹ However, for $\text{Ge}_{1-x}\text{Sn}_x$ to be useful in devices it would typically require substitutional Sn concentrations of at least 5%.² A further important feature of $\text{Ge}_{1-x}\text{Sn}_x$ (hereafter referred to as GeSn) is that substitutional Sn concentrations in the region of 7%–8% can convert Ge from an indirect into a direct bandgap semiconductor,^{3–6} thereby making the construction of GeSn lasers^{7,8} feasible and could open the door to Group IV, Si-based optoelectronic devices. Clearly, GeSn is an interesting material which may find a variety of applications in future microelectronic devices.

Unfortunately, the growth of epitaxial GeSn is extremely challenging. Tin has a low melting point of 232 °C which limits the growth temperature, while its diamond phase, α -Sn, is only stable at temperatures below 13 °C. This, together with the large 15% mismatch between Sn and Ge, its tendency for surface segregation, and the very low Sn equilibrium solubility (<1% at room temperature), makes it difficult to grow GeSn epitaxially on Ge substrates at concentration levels where the desirable features of GeSn become available. The net result is that epitaxial GeSn can only be grown under non-equilibrium conditions. After considerable effort, epitaxial growth techniques have now improved to the point where it is

possible to grow strained epitaxial GeSn layers (on Ge, on a Ge buffer on Si, or directly on Si) with an Sn concentration of technological interest using low temperature molecular beam epitaxy,^{9–12} chemical vapour deposition,^{13,14} or solid phase epitaxy¹⁵ techniques.

Clearly, GeSn grown under non-equilibrium conditions will be metastable, and probably even more so when grown in the form of strained layers. Given that the material will be subjected to various heating stages during device manufacturing, it is important to establish the stability of the strained layers (with regards to both strain and Sn solubility) when subjected to thermal annealing. In this regard, a number of thermal studies have been undertaken. Vincent *et al.*¹³ found that 40-nm thick GeSn layers with 8% Sn could withstand (i.e., remain fully strained) thermal treatments of 500 °C for 10 min, but after 30 min at the same temperature some Sn-Ge interdiffusion was observed by secondary ion mass spectroscopy. A similar observation was made by Asano *et al.*¹⁶ who showed that when 200-nm thick GeSn layers with Sn concentrations of 3.4% and 4.6% were subjected to post-deposition annealing, relaxation set in at temperatures above 500 °C, and the higher the concentration the lower the temperature and the shorter the annealing time required for relaxation to occur. Upon annealing at 600 °C they observed Sn precipitates on the surface of the GeSn layers. Recently, Kumar *et al.*¹⁷ used atom probe tomography to monitor Sn cluster formation during the GeSn layer relaxation. Although they found that Sn clusters formed during thermal anneals in the range of 580–640 °C they could find no correlation between Sn-cluster formation and the degree of relaxation, which led them to conjecture that the main relaxation mechanism must

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be via defect generation, such as misfit dislocations, threading dislocations, etc.

Strain relaxation in 160-nm thick GeSn layers with a 7.8% Sn content has been thoroughly investigated by Li *et al.*¹⁸ where they were subjected to rapid thermal annealing for 40 s at temperatures ranging from 300 to 620 °C. Using a combination of X-ray diffraction (XRD) about the (004) reflection and reciprocal space maps about the (224) reflection, they were able to extract the perpendicular and parallel components of the GeSn lattice constant, from which they could determine the degree of relaxation in the GeSn layer. The relaxed GeSn “bulk” lattice constant was then determined from the perpendicular and parallel components assuming that the GeSn Poisson ratio was independent of Sn concentration. (It should be noted, however, that other authors^{15,19,20} indicate that the Poisson ratio is in fact Sn concentration dependent.) Although Li *et al.* had no direct information on the substitutional Sn concentration in the strained layer they were able to deduce it indirectly from the bulk lattice constant using the composition dependent model put forward by Gencarelli *et al.*¹⁹ This enabled them to conclude that at temperatures below 400 °C the GeSn layers remained fully strained. With temperatures rising from 420 to 540 °C the degree of relaxation increased to ~40%, without any change in the Sn content of the GeSn film. As the temperature was raised further, initially to 580 °C and then to 620 °C, the Sn concentration decreased and the layer became completely relaxed. In addition, cross-sectional transmission electron microscopy showed the appearance of misfit dislocations during the period of gradual relaxation (420–540 °C) while energy-dispersive X-ray measurement exposed Sn precipitation after complete relaxation, both as clusters within the GeSn layer and also the formation of an Sn rich layer at the surface of the sample. From all of this, Li *et al.* concluded that the formation of misfit dislocation is the dominant mechanism for strain relaxation.

Although the model proposed by Li *et al.*¹⁸ is consistent with the results of Kumar *et al.*,¹⁷ they provide no direct evidence that the relaxation takes place without Sn expulsion from the lattice and given Sn’s low solubility in Ge, together with the non-equilibrium nature of the GeSn layers, it is surprising that Sn remains so firmly bound in the GeSn lattice during the relaxation process. In this regard, it should be noted that the use of XRD to determine both the substitutional Sn content and the elastic strain (relaxation) has a number of intrinsic limitations, namely (i) the technique averages over the depth probed, (ii) the values deduced depend on the validity of the model employed, and (iii) XRD provides information on the coherent parts of the sample while ignoring the disordered regions. Furthermore, the lattice parameters measured with XRD will be affected by both the misfit dislocations and the Sn expulsion—which can take place simultaneously—making interpretation difficult. While Gencarelli *et al.*²¹ have shown that it is possible to obtain local information on the Sn configuration by extended X-ray absorption fine structure, linking the local defect structure to elastic strain remains complex.

To this end we have revisited this topic employing Rutherford backscattering spectrometry (RBS), together with

channelling. With RBS one is able to directly measure the Sn composition without the need for modelling. Furthermore, channelling along an off-normal axis enables one to determine the strain in the GeSn layer^{22,23} (directly measuring the tetragonal distortion—irrespective of the relaxation mechanism, be it precipitation and/or misfit dislocations), together with the Sn substitutional fraction²⁴ in the GeSn lattice. While channelling with RBS is in many respects a complementary technique to XRD, it does have the significant advantage of being able to provide a direct and independent measure of strain, together with the Sn concentration, its distribution within the layer, and its location in the GeSn lattice. All of this is obtained without the need to resort to a model and it is thus ideally suited for such a study.

EXPERIMENTAL DETAILS

Metastable GeSn layers with an Sn concentration of 6.5% and thickness of 80 nm were grown at 320 °C by chemical vapour deposition onto a Ge(100) virtual substrate^{13,14} (i.e., a 1 μ m fully relaxed Ge layer grown on a Si(100) substrate). No capping was applied to the GeSn layer to prevent Sn evaporation during the thermal anneals as the capping might have interfered in the relaxation process. Instead, the total amount of Sn in the film was carefully monitored by RBS to determine if any Sn evaporation occurred during the thermal anneals. The wafer was diced into smaller samples which were then annealed for 20 min at temperatures ranging from 300 °C to 700 °C in a vacuum furnace (pressure $\sim 10^{-5}$ Pa). Incorporation of Sn in the Ge increases the size of the unit cell. When the GeSn layer is grown pseudomorphically on a Ge substrate, strain is introduced causing the unit cell to be distorted along the normal direction which can be assessed by X-ray diffraction (XRD). The XRD investigation was carried out at room temperature with a Bruker D8 X-ray diffractometer equipped with a Cu source. The increased spacing between the (100) planes was obtained by comparing the (400) reflection from the GeSn layer with that of the Ge substrate. By determining the interplanar spacing in the GeSn layer of the annealed samples, one is therefore able to establish the temperature at which relaxation of the layer sets in.

Following the XRD analysis the samples were subjected to RBS/channelling using 2.80 MeV alpha particles, with the energy selected to provide good separation between the Sn RBS peak and the front edge of the Ge signal when the detector was placed at a backscattering angle of 150°. Because of the distortion arising from the incorporation of Sn the off-normal axes in the GeSn film no longer align with those in the underlying Ge substrate, which can be observed when channelling along off-normal axes (see Figure 1).

In this investigation, angular scans were conducted about the [110] axis (positioned 45.00° away from the [100] axis in a fully relaxed diamond lattice) using three energy windows, two of which represent the RBS signal of Sn and Ge from the GeSn film, and the third window Ge from the substrate. From the angular difference $\Delta\theta$ between the positions of the [110] axes in the GeSn and the Ge substrate (i.e., the minima in the angular scans of the Sn and Ge signal in

FIG. 1. Off-normal channelling geometry showing the misalignment ($\Delta\theta$) between the $[110]$ axis in a GeSn strained layer and the $[110]$ axis in the Ge substrate. The misalignment is the consequence of the increased spacing between the planes in the strained layer, which is the feature detected by XRD.

the film and that of the Ge in the substrate), the tetragonal distortion $\epsilon_T = \epsilon_{\parallel} - \epsilon_{\perp}$ can be determined²⁵ via

$$\epsilon_T = \frac{\Delta\theta}{\sin\theta \cdot \cos\theta}, \quad (1)$$

where θ is 45° for channelling along the $[110]$ axis. This provides a direct measure of the elastic strain incorporated in the film and enables one to establish if any relaxation has occurred in the GeSn film as a result of the thermal anneal.

Furthermore, a comparison of the Sn random RBS signals obtained before and after the thermal anneal reveals if any redistribution of Sn towards the sample surface or towards the GeSn/Ge interface has taken place, while a comparison of their channelled Sn RBS signals establishes if any Sn has been expelled from substitutional lattice sites. With regards to the latter measurements, it should be emphasized that channelling measurements along only one crystallographic direction are insufficient to determine the lattice site.²⁶ In our study, aligned and random spectra about the $[100]$ axis and the $[110]$ axis were therefore collected from all the samples. In addition, for two samples, namely, those annealed at 475°C and 650°C , channelling was also undertaken along the $[111]$ axis. For none of the samples could any significant difference in either the value of the minimum yield or Sn distribution be detected, irrespective of the axis that was used to derive these quantities. The results obtained for channelling along the $[110]$ axis, to be presented below, can thus be taken as being representative. From a comparison of the minimum yield, $\chi_{\min}$, of the Sn signal with that of the Ge signal in the GeSn layer, the Sn substitutional fraction can be estimated²⁷ from

$$f_{\text{Sn}} = \frac{1 - \chi_{\min}^{\text{Sn}}}{1 - \chi_{\min}^{\text{Ge}}}. \quad (2)$$

RESULTS

A preliminary RBS analysis of the “as-grown” sample, taken with a tilt angle 5° off the $[100]$ axis, showed that the thickness of the GeSn film grown on the Ge virtual substrate is 80 nm and the Sn composition of the film around 6.5% and uniformly spread throughout the GeSn film. The as-grown and annealed samples were then subjected to an XRD analysis. The effect of the thermal anneal on the (400) XRD reflections obtained from GeSn, Ge, and Si is presented in Figure 2. (Note: as no monochromator was used in this study, both the $K_{\alpha 1}$ and $K_{\alpha 2}$ diffractions are observed in the spectra presented below.) In the spectrum from the as-grown sample shown at the bottom of the figure the GeSn (400) peak appears around 64.8° , clearly separated from that of the Ge (400) substrate peak.

Initially, as the temperature of the thermal anneal increases, there is no change in the position of GeSn (400) peak. However, once the annealing temperature rises above 400°C the peak shifts toward the Ge (400) peak position, indicating that the GeSn interplanar spacing has decreased and thus that the strained GeSn layer has begun to relax. As the temperature is raised further, the GeSn (400) peak position continues to shift to

FIG. 2. XRD spectra of the (400) reflection from the GeSn layer, the Ge virtual substrate, and the Si substrate for the as-grown sample, together with those following 20 min anneals at temperatures indicated.

higher angles in a regular manner until a temperature of 600 °C, at which stage the GeSn (400) peak position (65.2°) is nearly that expected for a strain-free layer of this composition. Annealing at 650 °C for 20 min results in significant shift in the peak (and after the 700 °C anneal it has almost completely merged with the Ge peak).

To obtain a deeper understanding of the relaxation process the as-grown and annealed samples were then subjected to channelling-RBS. An angular scan taken along the $\langle 100 \rangle$ plane around the $[110]$ axis is shown in Figure 3(a), together with random and channelled spectra in Figure 3(b). As mentioned earlier, three sets of energy windows were used during the angular scan; the first set over channels 360–380 collected particles backscattered from the Ge substrate, the second (channels 390–410) those backscattered from Ge in the GeSn film, and the third (channels 420–440) from Sn in the GeSn film. The angular scans from the latter two are symmetric and the centre of the dip was determined by fitting a Gaussian function to the data. The angular scan from

substrate Ge is asymmetric as a result of the steering effect, whereby the incident flux of alpha particles channelled in the GeSn film enters the Ge substrate at, or less than, the critical angle and is then “steered” into the substrate axial channel (the half-width for axial channelling along the Ge $[110]$ axis at 2.8 MeV is $\Psi_{1/2} = 0.57^\circ$). Consequently, enhanced ion channelling in the substrate is observed at the axis position of the overlying GeSn layer. The position of the minimum in the substrate Ge scan has therefore been determined by fitting a smooth “spline” curve through the Ge substrate data. The data presented in Figure 3(a) show that the minima obtained from the GeSn film differ from that of the Ge substrate by 0.60° , thereby indicating that the GeSn film is under strain. From the angular offset, the tetragonal distortion for the as-grown GeSn is determined to be $\sim 2.1\%$.

Figure 3(b) shows a random spectrum taken in the vicinity of the $[110]$ axis together with two aligned spectra, one with the incoming beam aligned with the $[110]$ axis of the GeSn film (y-axis set at 44.40°) and the other aligned with $[110]$ axis of the Ge substrate (y-axis 45.00°), i.e., the angular positions indicated by the vertical dashed lines in Figure 3(a). The three vertical arrows in Figure 3(b) indicate the channel/energy for backscattering from the three elements, were they to be located at the surface of the sample. The symmetric random RBS peak observed around channel 430 arises from the Sn which is evenly distributed in the uppermost strained GeSn layer, while the shoulder on the high energy side of the Ge signal (indicated by the single horizontal arrow) arises because the Ge concentration in the GeSn layer (93.5%) is lower than that in the Ge substrate. Comparison of the two aligned spectra clearly shows that when the beam is aligned with the $[110]$ axis of the GeSn film the channelling is better in the film and worse in the Ge substrate, and vice versa when aligned with $[110]$ axis of the Ge substrate. (From the aligned spectrum it is very easy to distinguish between the Ge in the GeSn layer and that of the Ge substrate, which proved useful for the selection of the Ge energy windows.) When the incoming beam is aligned with the GeSn $[110]$ axis the Sn minimum yield is 18%, which is higher than one would expect for a perfect crystal. From the Ge and Sn minimum yields the Sn substitutional fraction in the as-grown GeSn film is found to be $f_{\text{Sn}} = 1.00 \pm 0.05$, indicating that essentially all the Sn in the film is located on lattice sites, and thereby suggesting that the overall quality of the GeSn crystallinity, rather than interstitial Sn, is mainly responsible for the poor Sn minimum yield.

Angular scans along the $[110]$ axis were performed on all the samples which had been subjected to a 20 min thermal anneal at temperatures ranging from 300 to 700 °C. The result obtained after the 475 °C anneal (Figure 4(a)) shows that the angular offset (i.e., the angular difference between the two sets of axes) has reduced to 0.37° thereby indicating the GeSn layer is now partially relaxed. Figure 4(b) shows that the GeSn layer is almost completely relaxed after the 600 °C anneal with an angular offset of only 0.10° .

The tetragonal distortion, ϵ_T , derived from the angular offset of the Sn minimum, is plotted as a function of annealing temperature in Figure 5 using black filled circles (●). (Note that the dashed line drawn through the circular points

FIG. 3. (a) Angular scans about the $[110]$ axis with gates set on (i) Ge in the substrate, (ii) Ge in the GeSn film, and (iii) Sn in the GeSn film. (b) Random spectrum in the vicinity of the $[110]$ axis, together with spectra obtained with the beam aligned with the $[110]$ axis of the Ge substrate (red triangles) and with the $[110]$ axis of the GeSn film (blue circles). Inset shows expanded plots of the Sn peak over channels 420–450.

FIG. 4. Angular scans about the [110] axis after the sample had been subjected to a 20-min thermal anneal at (a) 475 °C and (b) 600 °C.

is not a fit to a model, but is merely intended to act as a guide to the eye when assessing the trend.) The plot shows that essentially no relaxation occurs for anneals at temperatures of 400 °C or less, but it sets in rapidly once the annealing temperature exceeds this, and that the GeSn layer is essentially completely relaxed after anneals at temperatures of

FIG. 5. The GeSn tetragonal distortion (●) and the Sn substitutional fraction (▲) as a function of the annealing temperature. (Note: the Sn substitutional fraction data are dealt with later in the paper.)

650–700 °C. The results are therefore consistent with those reported earlier in the XRD analysis (Figure 2).

The additional advantage of channelling-RBS analysis is that it is also able to monitor the movement of Sn atoms into or out of substitutional lattice sites, and also detect any redistribution of Sn within the layer. It is thus far better placed to provide insight into how the relaxation process takes place. In Figure 6(a) the GeSn [110] aligned and random spectra from the Sn region after the 475 °C anneal are compared with those obtained for the as-grown sample. The two near-identical random spectra indicate that there has been essentially no Sn redistribution within the GeSn layer, while the similarity between the aligned spectra also indicates that the Sn in the layer remains firmly bound in lattice sites—as confirmed by the Sn substitutional fraction of 1.01 ± 0.05 . This is a little surprising given that Figure 5 shows that following the 475 °C anneal the GeSn layer is around 40% relaxed. From the same Figure 5 one can see that the GeSn layer is almost completely relaxed after the 600 °C anneal, yet the random spectra presented in Figure 6(b) again

FIG. 6. Comparison between GeSn [110] random and aligned spectra from the as-grown sample with those after a 20-min thermal anneal at (a) 475 °C and (b) 600 °C.

shows that very little Sn redistribution has taken place within the GeSn layer. The slight increase in the yield of the 600 °C aligned spectra indicates that a small amount of the substitutional Sn has been expelled from the lattice in the upper most region of the layer where the Sn substitutional fraction has now dropped to 0.92 ± 0.05 .

After the 650 °C thermal anneal (see Figure 7(a)) the Sn random RBS spectrum is no longer symmetrical implying that some redistribution of Sn in the GeSn layer has occurred during the thermal anneal. The total amount of Sn in the layer however remains constant, indicating that no Sn has been lost by evaporation. Comparison of the two aligned Sn RBS spectra in the same figure shows that there has been a further increase in the number of Sn atoms expelled from the lattice, and that this interstitial Sn mainly resides in the upper half of the GeSn film where the Sn substitutional fraction is now only around 0.70.

Figure 7(b), taken after the 700 °C anneal, shows that the Sn random spectrum has become even more asymmetrical and now exhibits an extended tail. This tail makes a

comparison of the Sn random spectra difficult but it is estimated that up 4% of the Sn could have been lost from the layer during the 700 °C thermal anneal. The tail of Sn RBS spectrum can either originate from Sn that has diffused back into the Ge substrate, or from Sn which has agglomerated in beads at the surface of the sample. Scanning electron microscopy (SEM) analysis of the samples annealed at these high temperatures confirmed the presence of Sn-rich beads on the sample's surface, together with what appears to be pits in the surface and broad hillocks, for the sample annealed at 700 °C (Figure 8). The minimum yield of the aligned spectrum has now risen to 70% in the near surface region where the Sn substitutional fraction decreased further to 0.35, indicating that most of the Sn in this region of the layer is now non-substitutional. The full set of Sn substitutional fraction values, plotted in Figure 5 (blue triangles), shows that within experimental error the Sn substitutional fraction remains close to unity up to and including 575 °C, and then rapidly decreases.

It is interesting to note that after the majority of the Sn had been expelled from the lattice following the 700 °C anneal the Ge minimum yield in the GeSn layer actually improved from around 18% to 10%, which suggests that the remaining GeSn lattice rapidly re-orders itself after the expulsion of the Sn from the lattice. One further feature worth noting is that the annealing temperature at which substantial Sn expulsion from the lattice is first observed by RBS (viz., 650 °C) coincides with the abrupt shift in the GeSn XRD peak position in Figure 2.

DISCUSSION

Both the XRD and the channelling-RBS investigation give consistent results regarding the thermal stability of the GeSn strained layers, namely, that the layers are stable at annealing temperatures up to (and including) 400 °C, but once this temperature is exceeded relaxation of the layer sets in and thereafter proceeds fairly rapidly. The evidence provided by the RBS investigation clearly shows that the initial relaxation took place without any Sn expelled from the lattice, nor being redistributed within the lattice. This suggests that the issue of Sn solubility in Ge is not the main cause of the relaxation but it is rather the inability of the GeSn layer to cope with the stress residing in the layer, which it then

FIG. 7. Comparison between GeSn [110] random and aligned spectra from the as-grown sample with those after a 20-min thermal anneal at (a) 650 °C and (b) 700 °C.

FIG. 8. Tilted SEM micrograph showing the presence of Sn-rich beads on the surface of the sample after a 20 min thermal anneal at 700 °C.

relieves by the introduction of misfit dislocation at the GeSn/Ge substrate interface or other defects. As the annealing temperature is raised, more defects are introduced and the layer relaxes further; however, the Sn solubility in the GeSn layer becomes an issue only at much higher temperatures.

It is only after the sample has been annealed at 600 °C for 20 min, i.e., when the layer is nearly completely relaxed, that one finds the first indication of some Sn having been ejected from the lattice (Figure 5). Significant Sn expulsion and redistribution within the layer only occurs following anneals at 650 and 700 °C. The channelling spectra suggest that most of the Sn expulsion takes place closer to the surface of the sample, but it cannot be ruled out that the non-substitutional Sn observed in this region had taken place deeper down and then moved rapidly towards the surface region. Clearly, as the Sn is ejected from the lattice it leaves the remaining GeSn lattice more Ge rich. Thus, during the 650 °C and 700 °C anneals the GeSn lattice is effectively in the process of converting into a more Ge-like lattice, and this accounts for the abrupt shift in the position of GeSn XRD peak towards the Ge substrate peak. The interstitial Sn formed by the expulsion then diffuses to the surface where it forms Sn rich beads, also reported by other investigators.^{16,18}

The results obtained in this investigation are therefore consistent with those of Li *et al.*¹⁸ and the unambiguous RBS evidence acquired in this investigation thus vindicates the method employed in their analysis of the data. It should be pointed out, however, that both Li *et al.* and our investigation were carried out on GeSn strained layers of roughly similar Sn concentration which were grown on Ge-buffered Si wafers. The process by which relaxation occurs may differ for GeSn strained layers with a higher Sn concentration, or for layers grown on Ge single crystal substrates.

CONCLUSION

A combination of channelling-RBS and XRD has been employed to gain insight into the manner in which a strained GeSn layer (containing 6.5% Sn) relaxes when subjected to thermal annealing. The investigation shows that the GeSn strained layer is thermally stable up to 400 °C, while above this temperature the layer begins to relax. Throughout almost the entire relaxation process the Sn remains substitutionally incorporated within the GeSn lattice, thereby indicating that it is not the limited Sn solubility in Ge which gives rise to the relaxation, but rather it is the inability of the GeSn lattice to withstand the internal stress that induces the relaxation. Finally, near the end of the relaxation process, the Sn is expelled from the GeSn lattice and diffuses towards the surface, while the remaining lattice rearranges and reorders itself epitaxially on the Ge-buffered substrate. Given that there is little strain residing in the lattice when Sn expulsion takes place also suggests that the Sn solubility in the lattice is not significantly impacted by the lattice strain.

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- ¹R. Loo, B. Vincent, F. Gencarelli, C. Merckling, A. Kumar, G. Eneman, L. Witters, W. Vandervorst, M. Caymax, M. Heyns, and A. Thean, *ECS J. Solid State Sci. Technol.* **2**, N35 (2013).
- ²B. Vincent, Y. Shimura, S. Takeuchi, T. Nishimura, G. Eneman, A. Firrincieli, J. Demeulemeester, A. Vantomme, T. Clarysse, O. Nakatsuka, S. Zaima, J. Dekoster, M. Caymax, and R. Loo, *Microelectron. Eng.* **88**, 342 (2011).
- ³R. Chen, H. Lin, Y. Huo, C. Hitzman, I. Kamins, and S. Harris, *Appl. Phys. Lett.* **99**, 181125 (2011).
- ⁴J. Mathews, R. T. Beeler, J. Tolle, C. Xu, R. Roucka, J. Kovetakis, and J. Mendendez, *Appl. Phys. Lett.* **97**, 221912 (2010).
- ⁵S. Gupta, B. Magyari-Kope, Y. Nishi, and K. C. Saraswat, *J. Appl. Phys.* **113**, 073707 (2013).
- ⁶W. Du, S. A. Ghetmiri, B. R. Conley, A. Mosleh, A. Nazzal, R. A. Soref, G. Sun, J. Tolle, J. Margetis, H. A. Naseem, and S.-Q. Yu, *Appl. Phys. Lett.* **105**, 051104 (2014).
- ⁷S. Wirths, R. Geiger, N. von den Driesch, G. Mussler, T. Stoica, S. Mantl, Z. Ikonik, M. Luysberg, S. Chiussi, J. M. Hartmann, H. Sigg, J. Faist, D. Buca, and D. Gruzmaier, *Nat. Photonics* **9**, 88 (2015).
- ⁸Y. Shimura, S. A. Srinivasan, and R. Loo, *ECS J. Solid State Sci. Technol.* **5**, Q140 (2016).
- ⁹E. Kasper, J. Werner, M. Oehme, S. Escoubas, N. Burle, and J. Schulze, *Thin Solid Films* **520**, 3195 (2012).
- ¹⁰M. Oehme, K. Kostecki, M. Schmid, F. Oliveira, E. Kasper, and J. Schulze, *Thin Solid Films* **557**, 169 (2014).
- ¹¹E. Kamiyama, K. Sueoka, O. Nakatsuka, N. Taoka, S. Zaima, K. Izunome, and K. Kashima, *Thin Solid Films* **557**, 173 (2014).
- ¹²S. Su, W. Wang, B. Cheng, G. Zhang, W. Hu, C. Xue, Y. Zuo, and Q. Wang, *J. Cryst. Growth* **317**, 43 (2011).
- ¹³B. Vincent, F. Gencarelli, H. Bender, C. Merckling, B. Douhard, D. H. Peterson, O. Hanson, H. H. Henrichsen, J. Meersschaut, W. Vandervorst, M. Heyns, R. Loo, and M. Caymax, *Appl. Phys. Lett.* **99**, 152103 (2011).
- ¹⁴F. Gencarelli, B. Vincent, L. Souriau, O. Richard, W. Vandervorst, R. Loo, M. Caymax, and M. Heyns, *Thin Solid Films* **520**, 3211 (2012).
- ¹⁵R. R. Lieten, J. W. Seo, S. Decoster, A. Vantomme, S. Peters, K. C. Bustillo, E. E. Haller, M. Menghini, and J. P. Locquet, *Appl. Phys. Lett.* **102**, 052106 (2013).
- ¹⁶T. Asano, Y. Shimura, N. Taoka, O. Nakatsuka, and S. Zaima, *Solid-State Electron.* **83**, 71 (2013).
- ¹⁷A. Kumar, J. Demeulemeester, J. Bogdanowicz, J. Bran, D. Melkonyan, C. Fleischmann, F. Gencarelli, Y. Shimura, W. Wang, R. Loo, and W. Vandervorst, *J. Appl. Phys.* **118**, 025302 (2015).
- ¹⁸H. Li, Y. X. Cui, K. Y. Wu, W. K. Tseng, H. H. Cheng, and H. Chen, *Appl. Phys. Lett.* **102**, 251907 (2013).
- ¹⁹F. Gencarelli, B. Vincent, J. Demeulemeester, A. Vantomme, A. Moussa, A. Franquet, A. Kumar, H. Bender, J. Meersschaut, W. Vandervorst, R. Loo, M. Caymax, K. Temst, and M. Heyns, *ECS J. Solid State Sci. Technol.* **2**, P134 (2013).
- ²⁰R. Beeler, R. Roucka, A. V. G. Chizmeshya, J. Kouvetakis, and J. Menendez, *Phys. Rev. B* **84**, 035204 (2011).
- ²¹F. Gencarelli, D. Grandjean, Y. Shimura, B. Vincent, D. Banerjee, A. Vantomme, W. Vandervorst, R. Loo, M. Heyns, and K. Temst, *J. Appl. Phys.* **117**, 095702 (2015).
- ²²R. A. Minamisawa, D. Buca, H. Trinkaus, B. Holländer, S. Mantl, V. Destefanis, and J. M. Hartmann, *Appl. Phys. Lett.* **95**, 034102 (2009).
- ²³S. Wirths, Z. Ikonik, A. T. Tiedemann, B. Holländer, T. Stoica, G. Mussler, U. Breuer, J. M. Hartmann, A. Benedetti, S. Chiussi, and D. Grützmaier, *Appl. Phys. Lett.* **103**, 192110 (2013).
- ²⁴J. Haskell, E. Rimini, and J. W. Mayer, *J. Appl. Phys.* **43**, 3425 (1972).
- ²⁵K.-N. Tu, J. W. Mayer, and L. C. Feldman, *Electronic Thin Film Science* (Macmillan, New York, 1992), p. 177.
- ²⁶A. Vantomme, *Nucl. Instrum. Methods Phys. Res., Sect. B* **371**, 12 (2016).
- ²⁷W.-K. Chu, J. W. Mayer, and M.-A. Nicolet, *Backscattering Spectrometry* (Academic Press, 1978), p. 269.