

Structural and vibrational properties of $\text{Sn}_x\text{Ge}_{1-x}$: modeling and experiments

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Abstract

The effects of composition and macroscopic strain on the structural properties and lattice vibrations of $\text{Sn}_x\text{Ge}_{1-x}$ solid solutions (SSs) are investigated numerically, employing Tersoff empirical inter-atomic potentials, and experimentally. The calculations provide statistical distributions of bond lengths, pair correlation function and vibrational Raman spectra of the SSs. Using this approach, we are able to evaluate the tin-content-dependent shifts due to the local environment (i.e changes in the atomic mass and bond stiffness) and strain effects in the calculated Raman spectra and compare them to experimental data. The relative importance of the composition dependent effects of the local environment and strain for epitaxial layers of GeSn solid solutions is analysed.

1. Introduction

GeSn and GeSnSi, group IV based crystalline semiconductor solid solutions (i.e. alloys with continuous range of compositions) have been the object of intense research in the 21-st century [1-10]. The interest is related to the possibility of making a silicon-compatible direct band gap material with controlled lattice constant and band gap energy. These achievements would allow for the development of new optoelectronic devices, such as infra-red photodetectors, quantum emitters and modulators, which are the necessary ingredients for integrated photonics. Another potential application of these materials is in multi-junction solar cells. A great technological advantage is the possibility of epitaxial growth of GeSnSi alloys directly on silicon substrates. Because of the lattice constant mismatch between silicon, germanium and tin and the difference in their thermal expansion parameters, epitaxial layers of GeSn and GeSnSi alloys in many cases are strained. Moreover, post-growth treatment of the structures may change the strain state due to motion of misfit dislocations near the interfaces. Since the strain affects the electronic band structure, the deformation control is a key factor for the band gap engineering [1, 5, 11].

The structural properties and strain states of tin-containing epilayers of group IV semiconductors have been studied both experimentally and theoretically. X-ray diffraction and electron microscopy methods allow for high-precision determination of the lattice constant and composition, providing information concerning the uniformity of the epilayers and the misfit dislocation density. Along with these techniques, Raman spectroscopy, a non-destructive and sensitive technique, is often used to gain information on the composition and strain in GeSn and GeSnSi alloys by measuring the positions of characteristic phonon modes and performing an appropriate theoretical analysis [11-14]. On the theoretical side, several works have been performed for tin-containing group IV alloys, devoted to the calculation (mostly using *ab initio* methods) of equilibrium lattice parameters [1, 2, 4, 15-17] and electronic band structure [2, 5, 15, 18, 19]. Although *ab initio* methods are very powerful, they are also very expensive computationally and their application to disordered systems, such as random alloys, is limited to small crystallites, otherwise they have to be combined with an approximation scheme to reintroduce translational symmetry, e.g. [20]. At the same time, empirical potential models proposed by Stillinger and Weber [21] or by Tersoff [22] can be applied to larger systems and have

produced insightful results for alloy crystals, e.g. phonon-related thermal conductivity of $\text{Si}_x\text{Ge}_{1-x}$ crystals [23]. They are much less expensive in terms of computation time and well suited for modelling effects of strain relaxation in alloys where the end members have different lattice constants [24-26], as it is the case of the system under consideration in this work [11, 12, 27].

It is known that the Raman frequency shift in semiconductor solid solutions is affected by the composition and strain, which are not always independent [28, 29]. Indeed, these two effects on the position¹ of the Ge-Ge phonon peak (which is the main feature in Raman spectra of Ge-Sn alloys) are caused by (i) local atomic environment changes with composition and (ii) macroscopic (possibly composition-induced) strain and must be present simultaneously, as known for other (better studied) systems, such as Si-Ge [30]. In principle, these two effects can be separated by combining the results of Raman scattering and XRD measurements. The net effect on the Ge-Ge peak position can be written as:

$$\Delta\omega_{\text{Ge-Ge}} = \Delta\omega_{\text{composition}} + \Delta\omega_{\text{strain}} . \quad (1)$$

Equation (1) describes the deviation of the Raman peak with respect to unstrained Ge crystal at same temperature ($\approx 300 \text{ cm}^{-1}$ at 300 K). It is expected that the first term, $\Delta\omega_{\text{composition}}$ should be always negative because its nature is similar to the phonon confinement effect in nanocrystals. Indeed, a cluster of Ge atoms surrounded by much heavier tin atoms that do not support the Ge-Ge vibration mode looks like a small size nanocrystal and the allowed wavevector values for it should be finite. By virtue of the relaxation of the zero-wavevector selection rule, such a finite size effect leads to a downward shift of the confined phonon frequencies because of the negative curvature of the bulk phonon dispersion curves in germanium [31]. It is hard to estimate this effect analytically for random alloys, however, numerical lattice dynamic calculations allow for predicting its composition dependence [24, 26]. In contrast, the second term in **Eq. (1)** may have any sign because it depends on several strain components and, consequently, on the type of deformation [32].

A number of previous works [11, 12, 27, 33-35] attempted to extract the separate contributions of the two effects. These included Raman spectroscopy studies performed on (nominally) relaxed [27, 34] or fully strained [35] layers. It was

¹ The line shape and width are also affected but these are harder to quantify, in particular, to separate the homogeneous (related to lifetime) and inhomogeneous (related to disorder) contributions to the linewidth.

concluded that biaxial strain (induced by the substrate) yields an increase of the Ge-Ge mode frequency, i.e. leads to a partial compensation of the first term in **Eq. (1)**. This conclusion was confirmed by direct measurements on two groups of samples grown in a unique deposition system on two different types of substrates, either directly on Si (yielding relaxed Sn-Ge layers) or on top of a Ge buffer layer (strained Sn-Ge layers); indeed, a very distinct compositional dependence was obtained for these two groups [33].

The vibration modes that directly involve tin atoms, i.e. Sn-Sn ($\approx 190 \text{ cm}^{-1}$) and Ge-Sn ($\approx 260 \text{ cm}^{-1}$), are usually rather weak (especially the former) and it is hard to follow their compositional dependence, even though they have been registered in a number of works [8, 11, 13, 14]. Thus, systematic Raman studies of a set of GeSn samples with different composition, eventually extended to other fundamental vibration modes, in principle, can provide information about the composition, the presence of different kinds of bonds (Ge-Sn, Ge-Ge, Ge-Si, *etc.*) and the strain. However, theoretical support for the necessary analysis (solid solution's vibration mode dependence upon composition and strain) is rather scarce in the literature.

In this work, we present the structural properties and vibrational Raman spectra of $\text{Sn}_x\text{Ge}_{1-x}$ crystalline alloys, calculated using the Tersoff potential [22], extended to grey tin in **Ref. [36]**.² This family of semi-empirical potentials is known as quite appropriate and widely used for description of atomic bonds in group IV crystals with diamond structure [24, 25]. This approach allows us to obtain information on statistical distributions of bond lengths and angles between adjacent bonds. The former is discussed in comparison with the Vegard's law. We also evaluate the composition and strain dependent shifts in the Raman spectra and compare them with experimental results obtained for a set of Ge-Sn alloy epilayers grown by molecular beam epitaxy (MBE).

2. Modelling procedure

2.1. Building Sn-Ge crystallites

The algorithm used in this work is similar to the previously used by us for SiGe nanocrystals [24, 37]. First, $\text{Sn}_x\text{Ge}_{1-x}$ crystallites were built by randomly distributing xN tin and $(1-x)N$ germanium atoms over the sites of a diamond lattice structure. Bearing in mind the application of periodic boundary conditions, cubic crystallites

were used, $8 \times 8 \times 8$ unit cells (4096 atoms) for investigation of the structure and $5 \times 5 \times 5$ unit cells (1000 atoms) for the lattice dynamics and Raman spectra calculations.

The starting lattice constant was chosen according to Vegard's law:

$$a_{GeSn}(x) = a_{Ge}(1-x) + a_{Sn}x \quad (2)$$

where $a_{Ge} = 5.64613 \text{ \AA}$ and $a_{Sn} = 6.48920 \text{ \AA}$ are the lattice constants of the crystalline Ge and Sn, respectively. So far, the underlying lattice retained the T_d symmetry with perfect tetrahedral bonding.

The Tersoff potential was used to describe the interactions between the atoms, with the parameters listed in **Table 1**. Periodic boundary conditions were applied for the surface atoms. The lattice was allowed to relax to the minimum of its total energy by letting the atoms to move in response to the forces produced by their neighbours. For this relaxation, a molecular dynamics method employing the Verlet algorithm [38] was used. The equations of motion were integrated at each temporal step (not exceeding 10^{-15} s) until the equilibrium of the lattice was achieved. The crystallite, which no longer possessed the T_d symmetry (unless for $x = 0$ or 1) after the relaxation, was used for the statistical analysis of the distributions of bond lengths and angles.

2.2. Raman spectra

Given the atomic coordinates and the (Tersoff) potentials acting on each of them, the dynamical matrix of the crystallite (constituted by the second derivatives of the atomic potential energy with respect to the spatial coordinates at equilibrium) was obtained. The vibration modes (*i.e.* eigenmode frequencies and the corresponding eigenvectors, *i.e.* normalised atomic displacement vectors, \mathbf{u}_l^j , for the l -th atom and j -th vibration mode) were calculated by diagonalizing the dynamical matrix.

With these data, the non-resonant Raman spectra were calculated using the bond polarisability model [39], where three second-rank tensors are defined for each (j -th) phonon mode as follows:

$$\tilde{\alpha}_1^j = \sum_{l=1}^N \sum_{i=1}^4 \left(\hat{r}_{li} \otimes \hat{r}_{li} - \frac{\tilde{I}}{3} \right) (\mathbf{u}_l^j \cdot \hat{r}_{li}), \quad (3a)$$

$$\tilde{\alpha}_2^j = \sum_{l=1}^N \sum_{i=1}^4 \left[\frac{1}{2} (\hat{r}_{li} \otimes \hat{u}_l^j + \hat{u}_l^j \otimes \hat{r}_{li}) - \frac{\tilde{I}}{3} \right] (\mathbf{u}_l^j \cdot \hat{r}_{li}), \quad (3b)$$

² For tin, these parameters were adjusted to obtain the experimentally known value of the cohesion energy [36].

$$\tilde{\alpha}_3^j = \tilde{I} \sum_{l=1}^N \sum_{i=1}^4 (\mathbf{u}_l^j \cdot \hat{r}_{li}), \quad (3c)$$

In **Eqs. (3)** \hat{r}_{li} is a unit vector directed from atom l to its neighbour i , \hat{u}_l^j is a unit vector along the atomic displacement vector \mathbf{u}_l^j , and \tilde{I} is the unit dyadic. The tensor $\tilde{\alpha}_1$ represents the polarizability modulation due to bond stretching and is responsible, e.g., for the Raman peak of pure crystalline Ge at $\approx 300.9 \text{ cm}^{-1}$. The $\tilde{\alpha}_2$ and $\tilde{\alpha}_3$ contributions represent angular distortions and vanish in the case of perfect tetrahedral bonding, while they have to be taken into account for random-network structures characteristic of amorphous Si or Ge. Since the pair correlation function for our relaxed GeSn solid solutions (Fig. 4), showing well-defined peaks corresponding to the diamond lattice coordination spheres looks much alike that for the crystalline materials with diamond structure rather than for the amorphous materials, we may say that the tetrahedral symmetry of the underlying lattice is approximately preserved and it is expectable that the contribution of terms (3b) and (3c) may be neglected. Indeed, it was confirmed by our calculations for some alloy compositions. Moreover, the diagonal elements of the full polarizability tensor, $(\tilde{\alpha}_1 + \tilde{\alpha}_2 + \tilde{\alpha}_3)$, vanishing in the case of perfect tetrahedral bonding, were found to be very small.

Thus, the Raman scattering intensity, averaged over the possible cross-polarization configurations and normalized to the volume, was calculated as:

$$I(\omega) \propto \frac{[n_{BE}(\omega) + 1]}{N\omega} \sum_j \frac{(\alpha_{1xy}^2 + \alpha_{1xz}^2 + \alpha_{1yz}^2)}{3} \delta(\omega - \omega_j), \quad (4)$$

where $n_{BE}(\omega)$ is the Bose-Einstein function. For computational purposes, the δ -function in **Eq. (4)** was replaced by a Lorentzian. Such a procedure has been used before to model the Raman spectra of bulk pure Si and Ge, Si-Ge alloy and corresponding nanocrystals [17, 24, 40, 41]. In order to make the calculated spectra comparable to experimental ones, they were averaged over at least ten different realisations of alloy disorder for each value of x .

3. Calculated results

3.1. Bond length distribution

The average bond length, in first approximation, is described by the phenomenological Vegard's law, **Eq. (2)**. However, for the Sn-Ge system,

experimental results and calculations [1-3, 6, 17] show deviations, which are more substantial than for Si-Ge alloys. A better approximation for $\text{Sn}_x\text{Ge}_{1-x}$ alloys is provided by the following expression:

$$a_{\text{GeSn}}(x) = a_{\text{Ge}}(1-x) + a_{\text{Sn}}x + \theta(1-x)x, \quad (5)$$

where θ is called the slope parameter. Notice that experimental data exist only for $x < 0.2$, while the calculations go beyond this value of Sn content.

The calculated results obtained in this work, at zero temperature and with composition step, Δx , of 0.1 are shown in **Fig. 1**. The maximum deviation between the calculations and the Vegard's behaviour is reached for $x = 0.6$. The best fit of **Eq. (5)** to our calculated data (dashed line in **Fig. 1**) is obtained for the slope parameter $\theta = 0.026$ nm. Even though this value does not coincide with that obtained from experimental data [6], in general, our calculated results compare well with the literature data in this composition range.

Figure 2 shows the comparison of our calculated results with experimental data from the literature, in the range of alloy compositions $x < 0.2$, which is the important range for applications. Even here deviations from the Vegard's law are clearly noticeable and the experimental and calculated (including ours) data indicate a steeper growth of the average lattice parameter than predicted by **Eq. (2)**.

It is interesting and useful to analyse, separately, the lengths of different bonds, *i.e.*, Sn-Sn, Sn-Ge and Ge-Ge. These results are presented in **Fig. 3**, which demonstrates a three-modal distribution of bond lengths. It clearly shows that the relaxed Sn-Ge lattice is not a diamond crystal structure any more. Similar conclusions were derived for Si-Ge alloys [37] but for the tin-germanium system the effect is more pronounced because of the larger difference of the lattice parameter of α -Sn from that of Ge than in the case of silicon. It is also possible to conclude that the strongest variation with composition occurs for the Sn-Ge and Ge-Ge bonds, while Sn-Sn bond length is less dependent of x . The latter was also concluded in **Ref. [8]** where the authors found the strongest compositional variation for Ge-Ge bonds.

Another way to see the alloy disorder introduced by the substitution of germanium with tin atoms is provided by the "pair correlation function", which gives the probability to find a second atom within a spherical shell of radius, r , and thickness, dr , with the first atom in its centre. It is a measure of the alloy short-range order. The performed numerical calculations followed the procedure proposed in **Ref. [38]** and

the results are shown in **Fig. 4**, for $x = 0.2$. Each peak corresponds to a certain coordination sphere of the reference atom (either Ge or Sn). As it is seen from this plot, the short-range order is different for tin and germanium atoms only for the first coordination sphere (seen by the shift of the peak for Sn-Sn atomic pairs), that reflects the difference in the Ge-Ge and Sn-Sn bond lengths. For further coordination spheres, no such shift between Sn and Ge atoms is seen and the same behaviour is verified also for other compositions. This effect can be understood by a compensation of the bond length difference due to the variation of the inter-bond angles, another composition-dependent effect verified by our calculations. Notice that the broadening of the peaks is related to static alloy disorder only and not to thermal displacements of the atoms.

3.2. Calculated Raman spectra

Figure 5 presents the calculated Raman spectra of relaxed $\text{Sn}_x\text{Ge}_{1-x}$ solid solutions with different compositions, including $x = 0$ (pure germanium). The obtained spectra are considerably different from those obtained in **[24]** for $\text{Si}_x\text{Ge}_{1-x}$ system, using essentially the same model. Raman spectra of the Si-Ge system are characterised by three principal modes corresponding to the Ge-Ge, Si-Ge and Si-Si vibration (although a fine structure can be resolved, related to different local atomic arrangements **[42]**). For the Sn-Ge system (**Fig. 5**) the peaks corresponding to the vibrations involving Sn-Sn and Sn-Ge bonds are hardly seen for small and medium values of x . Indeed, as mentioned in the Introduction, experimental Raman spectra of this system are dominated by the Ge-Ge peak, while a weak Ge-Sn feature can also be observed, as it will be shown in **Section 4**. Moreover, in the calculated Raman spectra, the Ge-Sn peak appears as a shoulder of the main (Ge-Ge) mode and cannot be identified as a clear peak. This is because of the smoothening of the calculated spectra obtained for relatively small size supercells³ and averaging over at least 10 different realizations of alloy disorder. Nevertheless, it is seen that the role of the Sn-Ge feature increases with the increase of tin content. As for the Sn-Sn vibrations assigned by some authors as the origin of a rather broad, low intensity band observed around 185 cm^{-1} **[8, 11, 13, 14]**, the calculations performed in this work do not provide any evidence of this.

The peak position of the Ge-Ge band in the calculated spectra can be approximated by the following linear relation:

$$\omega_{\text{Ge-Ge}} = 300.9 - 91.6x \quad [\text{cm}^{-1}] \quad (6)$$

The coefficient in the linear term of Eq. (6) is close to the experimentally measured one (-83 cm^{-1}), in the low tin content range, $0 < x < 0.077$, for fully relaxed samples [33] and also to the value (-95 cm^{-1}) proposed by the authors of [12, 27], based on their analysis of strained layers and using the theoretical estimate of the strain contribution according to Ref. [32]. The latter is based on experimentally measured phenomenological deformation potentials, while our calculations employ Tersoff potentials, so the closeness of the values obtained from very different approaches makes us confident concerning the reliability of the obtained results.

The model reported here also allows for investigating the effect of macroscopic strain on the vibration modes of $\text{Sn}_x\text{Ge}_{1-x}$ alloys under elastic stress produced by some external forces. The strain was imposed by changing the supercell size in one, two or three directions (coinciding with the principal axes of the underlying diamond lattice). The deformation (assumed independent of composition) was counted with respect to the size corresponding to the average lattice constant value for the given composition x as presented in Fig. 1. The results for strained supercells are shown in Fig. 6 for several different types of deformation.

As it can be seen from Fig. 6, the position of the Ge-Ge peak and even the shape are strongly influenced by the macroscopic strain. The sign of the shift (with respect to the unstrained case, curve 1 in the plot) correlates with the sign of the trace of the strain tensor. Compressive strain (curves 2, 4 and 5) produces a blue shift that compensates or even overcomes the red shift caused by the tin doping (shown in Fig. 5). Indeed, the two terms in Eq. (1) have opposite signs in these cases. The physical cause of the mode shift here is that the imposed static displacements of the atoms change the force constants between them (determined by the Tersoff potentials). Again, we notice the qualitative agreement with the results predicted by the analytical theory using empirical deformation potentials [32]. The most realistic case in Fig. 6 is the one represented by curve 5, since for a Sn-Ge layer grown on a germanium substrate, the in-plane components ε_{xx} and ε_{yy} should be negative (compression)

³ For computational purposes each eigenmode was broadened by $\gamma=0.006 \text{ cm}^{-1}$, i.e. the δ -function in Eq. (4) was replaced by a Lorentzian of FWHM γ .

while ε_{zz} (also commonly denoted as ε_{\perp}) should be positive. In fact, the lattice constant in the growth direction, a_{\perp} (z axis), measured in **Ref. [33]** was larger than the equilibrium lattice parameter corresponding to the given Sn content.

4. Experimental results

4.1. Samples and experimental details

The samples were grown by molecular beam epitaxy using an electron beam evaporator for Ge with a silicon crucible and a Knudsen cell for Sn with pyrolytic BN crucible and a base pressure lower than 10^{-9} mbar [43-45]. The layers were grown on Si (100) wafers with 100 mm diameter. The wafer was treated with a HF-bath and introduced into the MBE chamber and heated, *in situ*, to 700 °C for a period of 5 minutes to remove the hydrogenised layer on its surface by thermal desorption. After this thermal treatment, a Ge epitaxial buffer layer with 100 nm thick was grown at 330 °C with a growth rate of 0.43 Å/s. Then, a GeSn layer, with a target thickness of 200 nm, was grown over the Ge buffer layer, at a substrate temperature between 75 and 85 °C. The Ge flux for the GeSn growth was the same as used for the buffer layer and kept constant for all the samples, whereas the Sn flux was changed from sample to sample. The samples were annealed *in-situ* by ramping-up their temperature to \approx 195 °C followed by an immediate ramp-down to room temperature. The very low and not usual substrate temperature (75-85 °C) used for the GeSn growth was chosen in order to avoid precipitation and / or segregation of Sn, since it is known that Sn has low solubility in Ge (\approx 0.5%). Samples with Sn content up to 4.3 % were grown so as to avoid significant changes of the lattice structure through defects or segregation or precipitation of Sn. The deposited epilayers were characterized using Rutherford backscattering spectroscopy (RBS) to determine the Sn content, X-ray diffraction (XRD) to determine the bond lengths (i.e. strain), transmission electron microscopy (TEM) to determine the quality of the layers, and the micro-Raman spectroscopy. **Table 2** provides a list of samples used in this study and the respective Sn contents determined using RBS. TEM showed no evidence of either segregation or precipitation of Sn atoms. Raman spectroscopy studies were performed using a 633 nm excitation in a backscattering geometry, at room temperature; the frequency shift was calibrated using a Si wafer.

4.2. XRD results and strain analysis

The XRD geometry usually employed to study epitaxial semiconductors with cubic structure is the geometry known as ‘one-dimensional $\omega/2\theta$ rocking curve’ of a certain diffraction plane. Using the angular position of the diffraction peak originated by the (004) planes and applying the Bragg’s law it is possible to determine the inter-planar distance, d_{004} , and therefore the perpendicular (or out-of-plane) lattice constant:

$$a_{\perp} = 4d_{004}. \quad (7)$$

The parallel (or in-plane) lattice constant, a_{\parallel} , in principle, can be determined from the position of a diffraction peak produced by another family of atomic planes, e.g. (224). Taking the growth plane as reference, the parallel (*in-plane*) and perpendicular (*out-of-plane*) diagonal components of the strain tensor can be defined through the lattice constants of the deformed layer and the relaxed lattice constant (a) as:

$$\varepsilon_{\perp} = \frac{a_{\perp} - a}{a}, \quad (8a)$$

$$\varepsilon_{\parallel} = \frac{a_{\parallel} - a}{a}. \quad (8b)$$

For a fully relaxed solid solution, the lattice constant usually follows a linear dependence upon the composition. This dependence (the Vegard’s law) has been verified for $\text{Sn}_x\text{Ge}_{1-x}$, $a(x) = a_{\text{Ge}}(1 + 0.147x)$ [35]. For the ultimate case of fully strained solid solution (so called pseudomorphic strain caused by the elastic force induced by the substrate with the same crystal structure but with a different lattice constant, see **Appendix**) one can expect $a_{\parallel} = a_{\text{substrate}}$ and, if the substrate is relaxed germanium crystal, $a_{\text{substrate}} = a_{\text{Ge}} = 0.5658$ nm. However, if the substrate (or the buffer layer) is deformed itself, a_{\parallel} is not known *a priori*.

The deformations (*i.e.* the out-of-plane and in-plane components of strain tensor) can be related using the elasticity theory for the case of pseudomorphic strain (see **Appendix**),

$$\varepsilon_{\perp} = -2 \frac{C_{12}}{C_{11}} \varepsilon_{\parallel}, \quad (9)$$

where C_{11} and C_{12} are the elastic constants of the material. Since the samples have a very low amount of Sn, the pure germanium values can be used for the calculations, for which **Eq. (9)** yields $\varepsilon_{\perp} \approx -0.7\varepsilon_{\parallel}$. In this way, by using the relation **(8b)**, information concerning the parallel (*in-plane*) lattice constant has been obtained.

A Cu source with characteristic emission $K\alpha_1$ (0.154056 nm) and $K\alpha_2$ (0.154439 nm) was used for the XRD measurements⁴. The XRD configuration used for this study was the standard $\theta/2\theta$ scan and the calibration was made with crystalline bulk silicon. Relevant information was obtained by analyzing the (004) diffraction peak. The diffractograms of the studied samples typically show two peaks, (i) $2\theta \approx 66^\circ$ associated with Ge-Ge bonds, and (ii) the one appearing between 65° and 65.5° , corresponding to (longer) Ge-Sn bonds.

For samples with low Sn content (#1 and #3) the latter is hardly seen, while it is quite evident for the samples with high Sn content (samples #4, #5 and #6).

We observed that for samples with lower Sn content, the Ge-Ge lattice constant is smaller than the one of a bulk Ge crystal, indicating that the layers are not fully relaxed but close to this. When the Sn concentration is large enough to originate the Ge-Sn diffraction peak, it was seen, by analysing the Ge-Sn peak position, that the changes in the lattice parameter are more significant and directly related to the Sn content, increasing with the increase of the Sn concentration. Since α -Sn lattice constant is bigger than that of Ge, the increase of the Sn content in the GeSn layer leads to an increase of the lattice parameter of the solid solution.

From the angular position of the (004) diffraction peak, obtained by fitting the diffractogram and using the Bragg's law, it is possible to determine the inter-planar distance, d_{004} , and then the out-of-plane lattice constant using **Eq. (7)**. As expected, we found that it increases with the increase of Sn content. Yet, we notice that the measured out-of-plane lattice constant for each Sn content is lower than the corresponding average lattice parameter value predicted by the Vegard's law, **Eq. (2)**. Using the lattice constant obtained through Bragg's law and the lattice constant of relaxed Ge crystal, the strain perpendicular to the GeSn layer has been calculated using **Eqs. (8)**. Upper limit of the in-plane strain can be evaluated using **Eq. (9)** (that assumes pseudomorphic strain). **Figure 7** shows the measured perpendicular strain values obtained for the samples #2, #3, #4, #5 and #6 as a function of the Sn content, the corresponding linear fit to these values and the line obtained by applying **Eq. (9)** to the latter (the upper limit of the in-plane strain). These results show that the linear variation of the measured out-of-plane deformation component with x , the slope of

⁴ Since the used system does not have a monochromator, the measured XRD spectra contain contributions of two Cu wavelengths ($K\alpha_1$ and $K\alpha_2$) for each diffraction peak. The XRD analysis was performed in the 2θ region between 24° and 69° , so both peaks were used to verify the analysis.

this line (≈ 0.028), is much smaller than the expected one for the case of pseudomorphic strain (≈ 0.103 , see **Appendix**). Thus, we conclude that our Ge-Sn layers are almost fully relaxed.

4.3. Experimental Raman spectra and their analysis

Figure 8 shows the Raman spectra obtained with the same acquisition conditions and normalized to the Ge-Ge phonon mode intensity, for three samples, bulk c-Ge (wafer), reference layer of germanium without Sn (#0) and GeSn sample #6 (the one with the highest Sn content). According to the previous studies [11-14, 27, 33-35], for this system it is expected to observe several Raman features, namely: (i) Ge-Ge phonon mode (near 300 cm^{-1}), either from the GeSn layers or from the Ge buffer layer or both, (ii) the TO-LO phonon mode of the Si substrate (521 cm^{-1}), (iii) a vibration mode due to the Ge-Sn bonds (around 260 cm^{-1}), and (iv) possibly a weak band around 185 cm^{-1} , which has been tentatively attributed to Sn-Sn vibrations by some authors [11], supported mostly by its proximity to the Γ point TO-LO phonon mode in grey tin [46].

From **Fig. 8** it is seen that the reference sample (without tin) exhibits the Ge-Ge phonon mode (the only one seen for the c-Ge) and also the bulk Si-Si phonon mode from the substrate ($\approx 520 \text{ cm}^{-1}$). The Si-Si mode is strong because this sample is thinner than the others (no GeSn layer, only the Ge buffer layer is present). Also seen is the Raman phonon mode at about 385 cm^{-1} assigned to the Ge-rich SiGe alloy. The presence of this Ge-Si phonon mode is probably related to the contamination of the buffer layer with Si due to the use of a silicon crucible for germanium precursor during the MBE growth.

Concerning the Raman spectrum of the GeSn sample #6, besides the Ge-Ge and the Ge-Si phonon modes it indeed exhibits two peaks (absent in the other samples' spectra), namely, peaks at ≈ 260 and $\approx 185 \text{ cm}^{-1}$ that we assign as above. Indeed, the Sn-Sn Γ point phonon peak position for α -Sn is $\approx 195 \text{ cm}^{-1}$ [46]. In Ge-Sn alloys with low tin content, the presence of the Sn-Sn mode can be attributed to small sized Sn clusters originating mechanical confinement effects, which results in a shift of the mode to lower frequencies, similar at what happens to phonons when confined in nanocrystals [31]. However, D'Costa *et al.* [27] expressed a different opinion: based on their polarized Raman spectroscopy studies, they associated this feature with a

disorder activated longitudinal acoustic (DALA) mode. In fact, the Sn-Sn mode does not show up in our calculated results even for considerably higher Sn contents (**Sec. 3.2**). The 260 cm^{-1} peak (Ge-Sn mode) is also too weak to help making any useful conclusions. Therefore, we shall concentrate on the Ge-Ge mode.

First, we notice that this mode in Ge buffer layer is almost not shifted with respect to relaxed germanium wafer (see inset in **Fig. 8**). This looks surprising since the buffer layer is strained, $\varepsilon_{\perp} \approx 0.15\%$ according to the XRD data. From the theory developed in **Ref. [32]** it follows (see **Appendix**) that the relative shift of this mode is related to the strain components as

$$\frac{\Delta\omega}{\omega_0} = -2.15\varepsilon_{\parallel} - 0.85\varepsilon_{\perp}. \quad (10)$$

Therefore, we are to conclude that the effects produced by the parallel and perpendicular strain components compensate each other in this case, which requires $\varepsilon_{\parallel} \approx -0.4\varepsilon_{\perp}$ (or slightly more if we take into account the 0.5 cm^{-1} blue shift yielded by fitting the Raman peaks). Thus, **Eq. (9)** is not valid and the pseudomorphic strain model does not apply to this layer.

Turning to the GeSn layers, their Raman spectra (of which only one is shown in **Fig. 8**) were fitted, in the vicinity of the Ge-Ge mode, and the obtained peak positions are presented by points in **Fig. 9**. Here both composition (i) and strain (ii) effects are present, yielding an increasing shift to lower wavenumbers as the Sn content increases. In general, the experimental data follow rather well **Eq. (6)**. It corroborates our conclusion that the studied GeSn layers are almost fully relaxed. Indeed, plugging $\varepsilon_{\parallel} = -0.147x$ and $\varepsilon_{\perp} = 0.103x$, characteristic of pseudomorphic strain into **Eq. (10)** we obtain for the strain induced term in Eq. (1):

$$\Delta\omega_{strain} = 67.1x \quad [\text{cm}^{-1}] \quad (11)$$

Some authors prefer to express this relation in the form $\Delta\omega_{strain} = k_{\varepsilon}\varepsilon_{\parallel}$, where the coefficient k_{ε} corresponding to **Eq. (11)** would be equal to -456.5 cm^{-1} . Experimentally, a somewhat lower value was obtained [**13**], $k_{\varepsilon} \approx -375 \text{ cm}^{-1}$. It should be noted, however, that the strain value in **Ref. [13]** was determined indirectly.

Using $\Delta\omega_{strain}$, from **Eq. (11)** and the composition contribution according to **Eq. (6)**, overall Ge-Ge Raman band shift versus Sn content in pseudomorphic-strained SnGe layers can be evaluated as

$$\omega_{\text{Ge-Ge}}^{\text{strained}} = 300.9 - 24.5x \quad [\text{cm}^{-1}]. \quad (12)$$

The dependence predicted by **Eq. (12)** is shown in **Fig. 9**. A similar weak dependence of the Ge-Ge peak position upon x for fully strained samples was reported in **Ref. [33]**. Raman studies performed on strained Ge-Sn solid solutions **[35]** revealed a linear relationship between the Ge-Ge phonon peak position and the Sn concentration with a much larger composition shift coefficient of -76.8 cm^{-1} . Assuming that their layers were *pseudomorphic*-strained led the authors of **Ref. [35]** to the suggestion of a very large composition effect for unstrained Ge-Sn solid solutions (shown by the dash-dotted line in our **Fig. 9**, which, to the best of our knowledge, has never been observed. As mentioned in **Sec. 3.2**, other authors **[12, 27, 33, 47]** reported much smaller (in modulus) values for the composition shift coefficient in relaxed samples, between -82 and -95 cm^{-1} . Our results, both calculated and experimental, support this estimate.

5. Conclusions

The calculated results obtained by applying semi-empirical Tersoff potentials to Ge-Sn alloys are in good qualitative agreement with the available low x experimental data and the results of DFT calculations. In particular, it applies to the deviations from the Vegard's law for the alloy lattice parameter. From the calculations one readily obtains further structural information such as the atomic pair correlation function and distributions of bond lengths and angles. Furthermore, studies of the lattice dynamics of alloys are possible since the dynamical matrix can be constructed in a straightforward way using the derivatives of the Tersoff potentials calculated in the new equilibrium positions of the atoms in the alloy. The proposed algorithm, here applied to tin-containing group IV solid solutions for the first time, also allows for studying strained alloys by directly imposing the desired deformation. It can be extended to ternary group IV alloys (experimentally investigated in **Ref. [11]**) or to quantum dot heterostructures **[48]**.

Applying the classical bond polarizability model **[39]**, we studied numerically the composition and strain effects on the principal (Ge-Ge) Raman mode of the alloys. Comparing the experimental results (**Fig. 9**) with the modelling ones obtained for this system without applying strain (see **Fig. 5**), a good agreement on the Ge-Ge peak position variation with the increase of the Sn content can be certified. Both the experimental and modelling results show a shift of the Ge-Ge mode to lower

wavenumbers, accompanied by an increase of the full width half maximum of the Raman mode with the increase of Sn. Our layers deposited on a Ge buffer layer are characterised by quite low strain (according to the XRD data). The composition shift (i.e. the vibration mode frequency change due to local changes of atomic mass and bond strength) is described by the numerically established **Eq. (6)**. However, in real samples that are epilayers, it is always accompanied by the second composition dependent effect caused by the macroscopic strain. It depends differently upon the in-plane and out-of-plane strain components. The lack of samples that are either fully relaxed (where all strain components are equal to zero) or pseudomorphic-stained (where the relation between the strain components is simple) leads to a rather broad range of composition shift coefficient values reported in the literature [33-35]. It also makes the quantitative comparison between the numerically calculated and experimental results difficult. Yet, the different examples of deformation shown in **Fig. 6** qualitatively agree with the trends predicted by the macroscopic theory [32]. Interestingly enough, the splitting of the Raman peak seen in **Fig. 6** for uniaxial traction (curve 6) was observed for Ge epilayers [49] and also for graphene [50]. With the help the macroscopic theory [32] it is possible to establish a simple numerical relation (**Eq. (11)**) between the strain effect and the composition. However, it should be used with care because of the complexity of the system from the point of view of the macroscopic elasticity theory and the pseudomorphic strain model may not be valid and $\Delta\omega_{strain}$ may have any sign depending on the relative value of the different components of the strain tensor. The understanding of the composition and strain contributions to the Raman peak shift will help achieving the properties needed, such as direct band gap in a Si-compatible group IV material, via composition and strain engineering.

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APPENDIX

Pseudomorphic strain and optical phonon frequency shift

Here we present some details concerning the pseudomorphic strain and also the essential part of the analytical theory for the strain induced Raman shift in a cubic crystal that was developed in **Ref. [32]**.

Pseudomorphic strain related to lattice mismatch between a film and a substrate can be described by the theory analogous to that of thermal expansion induced deformations. Non-zero stress components are given by **[51]**:

$$\sigma_{xx} = \sigma_{yy} = -\frac{Y}{1-\nu}\theta \quad (\text{A1})$$

where

$$\theta = \frac{a_{\text{Sn-Ge}}(x) - a_{\text{Ge}}}{a_{\text{Ge}}} = 0.147x \quad (\text{A2})$$

and $a_{\text{Sn-Ge}}(x)$ is the average lattice constant of the uniform Sn-Ge alloy with Sn content x , according to Vegard's law. In Eq. **(A1)**, Y and ν are the Young modulus and Poisson coefficient, respectively. For simplicity, the isotropic approximation is used, with

$$Y = \frac{(C_{11} + 2C_{12})(C_{11} - 2C_{12})}{C_{11} + C_{12}}, \quad (\text{A3})$$

$$\nu = \frac{C_{12}}{C_{11} + C_{12}}, \quad (\text{A4})$$

where C_{11} and C_{12} are the elastic constants of the crystal. Applying the generalized Hooke's law,

$$\varepsilon_{ik} = \frac{1}{Y} [(1-\nu)\sigma_{ik} - \nu \text{Tr} \hat{\sigma} \delta_{ik}], \quad (\text{A5})$$

one obtains:

$$\varepsilon_{xx} = \varepsilon_{yy} = -\theta, \quad (\text{A6a})$$

$$\varepsilon_{zz} = \frac{2\nu}{1-\nu}\theta. \quad (\text{A6b})$$

Thus we have:

$$\frac{\varepsilon_{\perp}}{\varepsilon_{\parallel}} = -\frac{2\nu}{1-\nu} = -2\frac{C_{12}}{C_{11}}. \quad (\text{A7})$$

The second equality uses cubic crystal elastic constants instead of the Poisson coefficient used for isotropic media and corresponds to **Eq. (9)** of the main text.

In **Ref. [32]** it is assumed that the strain affects the atomic vibrations only through the effective force constants that determine the vibrational frequencies. In the presence of elastic strain, the frequencies of optical phonons are given by the following secular equation:

$$\det \begin{vmatrix} p\varepsilon_{xx} + q(\varepsilon_{yy} + \varepsilon_{zz}) - \lambda & 2r\varepsilon_{xy} & 2r\varepsilon_{xz} \\ 2r\varepsilon_{xy} & p\varepsilon_{yy} + q(\varepsilon_{xx} + \varepsilon_{zz}) - \lambda & 2r\varepsilon_{yx} \\ 2r\varepsilon_{xz} & 2r\varepsilon_{yx} & p\varepsilon_{zz} + q(\varepsilon_{xx} + \varepsilon_{yy}) - \lambda \end{vmatrix} = 0, \quad (\text{A8})$$

where

$$\lambda = \Omega^2 - \omega_0^2 \quad (\text{A9})$$

with $\omega_0(\Omega)$ denoting the unshifted (shifted) optical phonon frequency and p , q and r are deformation potentials introduced in **Ref. [32]**. Thus, strain-induced shift is given by

$$\Omega - \omega_0 \approx \frac{\lambda}{2\omega_0}, \quad (\text{A10})$$

where λ is obtained by solving **Eq. (A8)**.

A simple example is hydrostatic strain/stress:

$$\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz} = \varepsilon \quad (\text{A11})$$

with

$$\lambda = (p + 2q)\varepsilon = -\gamma\varepsilon\omega_0^2 \quad (\text{A12})$$

$$\Omega - \omega_0 = -\gamma\varepsilon\omega_0, \quad (\text{A13})$$

where γ is the Grüneisen parameter, $\gamma = -(p + 2q)/6\omega_0^2$. So, we have a blue shift ($\Omega - \omega_0 > 0$) for compression ($\varepsilon < 0$) and a red shift for expansion ($\varepsilon > 0$).

For a biaxial strain with x , y and z axes along the principal axes [(001), *etc*] of the cubic crystal, all non-diagonal components ε_{ij} are equal to zero and one has from **Eq.**

(A8):

$$(\lambda - (p + q)\varepsilon_{\parallel} - q\varepsilon_{\perp})^2 (\lambda - 2q\varepsilon_{\parallel} - p\varepsilon_{\perp}) = 0 \quad (\text{A14})$$

So, two solutions exist:

$$\lambda_1 = (p + q)\varepsilon_{\parallel} + q\varepsilon_{\perp} \quad (\text{A15})$$

(double-degenerate) and

$$\lambda_2 = 2q\varepsilon_{\parallel} + p\varepsilon_{\perp} . \quad (\text{A16})$$

Here $\beta = (p - q)/2\omega_0^2$ is another dimensionless parameter. The parameters γ and β have been determined in [32]; for Ge $\beta \approx 0.23$ and $\gamma \approx 1$.

Expressing p and q in terms of γ and β we obtain:

$$\frac{\Omega_1 - \omega_0}{\omega_0} = -\frac{1}{3}(6\gamma - \beta)\varepsilon_{\parallel} - \frac{1}{3}(\beta + 3\gamma)\varepsilon_{\perp}, \quad (\text{A17})$$

$$\frac{\Omega_2 - \omega_0}{\omega_0} = -\frac{2}{3}(3\gamma + \beta)\varepsilon_{\parallel} - \frac{1}{3}(3\gamma - 2\beta)\varepsilon_{\perp}. \quad (\text{A18})$$

With strain components (A6), the singlet phonon mode (A16) corresponds to the displacement vector along z , while the doublet mode (A15) corresponds to the displacement vector within the x - y plane. If the Raman scattering experiment was performed in a backscattering geometry with the scattering vector $\Delta\vec{k} \parallel (001)$, then the singlet mode corresponds to LO phonon and the doublet represents two TO phonon modes. According to the selection rules for the (001) surface of a diamond crystal, scattering is precisely due to LO phonons [52] (so called $z(xy)\bar{z}$ configuration). Therefore, we should use Eq. (A18) to evaluate the strain-induced shift.

For low Sn contents all the parameters relevant here can be taken as for pure germanium, which are: $\gamma \approx 1$, $\beta \approx 0.23$ [32], $C_{11} = 1.29 \times 10^{12} \text{ dyn/cm}^2$ and $C_{12} = 0.48 \times 10^{12} \text{ dyn/cm}^2$ [53]. Substituting them into (A18) we obtain the numerical relation presented in the main text, Eq. (10). For pseudomorphic-strained GeSn $\varepsilon_{\parallel} = -0.147x$ and using (A7) we obtain $\varepsilon_{\perp} = 0.103x$, that yields Eq. (11).

Table 1: Tersoff potential parameters used in the present work.

	Ge, Ref. [22]	Sn, Ref. [36]
A (eV)	1769	2848
B (eV)	419.23	658.62
λ (\AA^{-1})	2.4451	2.25
μ (\AA^{-1})	1.7047	1.62
β	9.0166×10^{-7}	6.01×10^{-7}
n	0.75627	0.74
c	1.0643×10^5	1.4×10^5
d	15.6652	14.5
h	-0.43884	-0.502
R (\AA)	2.8	2.8
s (\AA)	3.1	3.2

Table 2: Sn content of the GeSn epilayers obtained by RBS.

Sample	Sn (at.%)
#0	0
#1	0.15
#2	0.20
#3	0.55
#4	1.68
#5	3.34
#6	4.30

Figure captions

Figure 1: Average lattice constant as a function of Sn content. Solid straight line represents the Vegard's law [Eq. (2)], rhombs are our calculated data and dashed line is Eq. (5).

Figure 2: Comparison of the average lattice constant in the region of low Sn contents. Solid straight line represents the Vegard's law [Eq. (2)], rhombs are our calculated data, squares are experimental data of Ref. [17], circles are experimental data of Ref. [6] and triangles and stars are Density Functional Theory (DFT) results for random [3] and partially ordered [1] Sn-Ge solid solutions, respectively.

Figure 3: Calculated bond length dependence upon Sn content for three types of bonds (Sn-Sn: rhombs, Sn-Ge: squares, Ge-Ge: triangles). Dashed line represents the Vegard's law, Eq. (2).

Figure 4: Pair correlation function for Ge-Sn solid solution with $x = 0.2$ calculated separately for Ge-Ge and Sn-Sn atomic pairs.

Figure 5: Raman scattering intensity calculated for relaxed $\text{Ge}_{1-x}\text{Sn}_x$ solid solutions of different compositions: (1) $x = 0$ (pure germanium), (2) $x = 0.05$, (3) $x = 0.10$, (4) $x = 0.15$, (5) $x = 0.20$.

Figure 6: Effect of different types of strain on the Raman band of $\text{Sn}_{0.1}\text{Ge}_{0.9}$: (1) $\varepsilon = 0$ (no strain), (2) $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz} = -0.01$ (hydrostatic compression), (3) $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz} = 0.01$ (isotropic expansion), (4) $\varepsilon_{xx} = \varepsilon_{yy} = -0.01$, $\varepsilon_{zz} = 0$ (compression in the plane of the layer), (5) $\varepsilon_{xx} = \varepsilon_{yy} = -0.01$, $\varepsilon_{zz} = 0.005$ (compression within the plane of the layer and expansion in the perpendicular direction), (6) $\varepsilon_{xx} = 0.01$, $\varepsilon_{yy} = \varepsilon_{zz} = 0$ (uniaxial traction). The axes x , y and z were chosen along the main crystallographic directions of the underlying diamond lattice.

Figure 7: Out-of-plane strain versus Sn content: points obtained from the XRD data for samples #2, #3, #4, #5 and #6 (rhombs) and pure Ge layer (full triangle), linear fit

to the experimental data for GeSn layers and calculated upper limit for the in-plane strain (dashed-dotted line). The open triangle represents the in-plane strain value for Ge buffer layer obtained from the Raman spectra analysis.

Figure 8: Raman spectra of the reference sample #0 (Ge), #6 (GeSn) and a relaxed Ge wafer.

Figure 9: Raman peak position of the Ge-Ge phonon mode as a function of Sn content of the GeSn samples; squares are the values obtained by peak fitting, the solid line is a linear fit to the experimental data represented by the squares, the dashed line (dotted line) represents calculated peak positions for fully relaxed (subjected to pseudomorphic strain) Ge-Sn solid solutions. The dash-dotted line is the linear dependence proposed by Rojas-Lopez *et al.* [35] for fully relaxed Ge-Sn layers. The triangle indicates the peak position for a bulk germanium crystal.

















