Decoupling the effects of composition and strain on the vibrational modes of GeSn semiconductors

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Abstract

We report on the behavior of Ge-Ge, Ge-Sn, Sn-Sn like, and disorder-activated (DA) vibrational modes in GeSn semiconductors investigated using Raman scattering spectroscopy. By using an excitation wavelength close to the \( E_1 \) gap, all modes are clearly resolved and their evolution as a function of strain and Sn content is established. Previous Raman scattering studies mainly focused on the Ge-Ge peak position which is insufficient to evaluate the effects of lattice strain and Sn content. Herein to decouple the individual contributions of content and strain, the analysis was conducted on a series of pseudomorphic and relaxed epitaxial layers with a Sn content in the 5–17 at.% range. The frequencies of all vibrational modes were found to display qualitatively the same behavior as a function of content and strain, that is a linear downshift as the Sn content increases or the compressive strain relaxes. Simultaneously, the Ge-Sn and Ge-Ge peaks broaden, and the latter becomes increasingly asymmetric. The behavior of the integrated intensity, width, and asymmetry of each one of these vibrational modes was also evaluated. We found that an increase in Sn content is associated with an increase in the relative integrated intensity of Ge-Sn and DA modes. The latter also increases as the layers become more compressively strained and become more prominent under the \( x(z)\bar{x} \) configuration as the intensity of the adjacent longitudinal optical modes decreases. The Raman mode asymmetry, coupled with the peak position, is exploited to implement an empirical approach to accurately quantify the Sn composition and lattice strain from Raman spectra.

Keywords: germanium-tin semiconductors, Raman spectroscopy, epitaxy, silicon photonics, vibrational modes, lattice strain, metastable semiconductors

(Some figures may appear in colour only in the online journal)

1. Introduction

Understanding the behavior of different vibrational modes in a semiconductor is of paramount importance to probe its crystal phase and symmetry, composition, lattice strain, isotopic content, electronic and phononic properties [1−3]. In this regard, Raman scattering spectroscopy has thus become a ubiquitous characterisation technique as information-rich spectra are acquired from straightforward and non-destructive measurements. Therefore, it is commonly used to evaluate the chemical composition and lattice properties of, for instance, group-IV semiconductors such as strained Si [4−6], strained Ge [7−10], SiGe [11−14], and GeSn layers [15−17]. The latter are particularly of growing interest because of their relevance to Si-compatible light emission and detection applications in the short- and mid-wavelength infrared, which can lead to the integration of optoelectronic and photonic circuits on complementary metal-oxide-semiconductor (CMOS) platforms [18−25].

Previous reports on the vibrational modes of GeSn mainly focused on the Ge-Ge longitudinal optical (LO) mode as the
analyses relied on the use of 488 nm [26, 27] or 532 nm [17, 28–33] excitation lines. Under these conditions, the signal-to-noise ratio is too low to clearly distinguish Sn-related vibrational modes in the vicinity of the more prominent Ge-Ge LO peak. This also applies to the study of ternary SiGeSn semiconductors [34–36]. When using a 633 nm excitation laser, the signal-to-noise ratio is significantly enhanced, thus allowing a clear distinction of the Ge-Ge and Ge-Sn modes, in addition to other features such as a disorder-activated (DA) and the Sn-Sn like modes. This higher sensitivity is attributed to the increase in Raman scattering cross section when the excitation wavelength becomes close to the material’s $E_1$ gap [34, 37]. Oehme et al [16] and D’Costa et al [15] provided a quantitative description of the evolution of peak positions as a function of the composition. However, in these studies, the investigated samples are either pseudomorphic [16] or relaxed [15]. Consequently, strain and compositional effects cannot be fully decoupled. In this work, we address this very issue by investigating the individual effects of strain and composition on the behavior of Ge-Ge, Ge-Sn, DA and Sn-Sn like vibrational modes in GeSn alloys using both pseudomorphic and relaxed layers with Sn contents in the 5–17 at.% range. This ability to distinguish the individual contribution of each parameter allows us to develop an approach to independently evaluate the strain and composition of GeSn layers from Raman measurements by exploiting the properties of vibrational modes and lattice disorder.

2. Experimental details

The investigated GeSn samples were grown on 0.6–1.1 μm-thick Ge virtual substrates (VS) on 4-inch Si (100) wafers in a low-pressure chemical vapor deposition (CVD) reactor, with ultra-pure H$_2$ as the carrier gas and 10% monogermane (GeH$_4$) and tin-tetrachloride (SnCl$_4$) precursors [21, 38]. The Sn content ($\gamma$), the residual in-plane strain ($\varepsilon$), and the degree of strain relaxation ($r$) for all layers listed in table 1 were estimated from high-resolution x-Ray Diffraction (XRD) Reciprocal Space Mapping (RSM) measurements, applying a bowing parameter of 0.041 Å [38, 39]. Micro-Raman scattering spectroscopy was performed using an InVia Raman Microscope from Renishaw with a 633 nm laser and an 1800/mm grating. In other studies, the use of a shorter wavelength laser was sometimes justified by the need for a shallower penetration depth to avoid the background signal from underlying Ge or GeSn buffer layers [34]. This is not a concern here even when a 633 nm excitation laser is used. Indeed, thicknesses measured from transmission electron microscopy (TEM) are larger than the laser penetration depth estimated from ellipsometry (∼30 nm for $y = 10$ at.%), meaning that a negligible contribution from the underlying layers to the measured Raman signal is expected. Thus, in partially relaxed layers only the top region of the sample with a uniform composition is probed by the laser [38]. While Voigt or Lorentzian functions are commonly used to fit Raman peaks [17], they cannot reproduce the asymmetric behavior that is typical to the Raman modes of semiconductor alloys [40, 41]. This asymmetry is due to alloying as the substitution of Sn atoms in the lattice breaks the translational symmetry and leads to a relaxation of the $\vec{q} = \vec{q}_c$ momentum selection rule [42]. To better reproduce the line shape of the LO modes, we employed exponentially modified gaussian (EMG) functions [15, 43]:

$$I(\omega) = I_0 + \frac{A}{2\pi} \left[ \exp \left( \frac{1}{2} \left[ \frac{w^2}{t} + \frac{\omega - \omega_c}{t} \right] \right) \left( \text{erf} \left[ -\frac{\omega - \omega_c}{\sqrt{2}w} \right] \right) + 1 \right]$$

(1)

where, $I_0$ is the intensity offset, $A$ represents the peak area, $w$ its width and $t$ is related to its asymmetry. For an asymmetric profile, the central frequency $\omega_c$ is different than the frequency at which the peak reaches its maximal value. Note that the extracted peak positions correspond to wavenumbers of maximal intensity. A fitting procedure was performed on the 200 cm$^{-1}$–360 cm$^{-1}$ range. After removal of the baseline, the line shape was fitted with three EMG functions. As for the Sn-Sn like mode, it was fitted with a single EMG.

Two sets of pseudomorphic and relaxed GeSn layers were investigated in this study, in addition to layers with intermediate strain relaxation. For the pseudomorphic GeSn series, a 4.0 at.% bottom layer (BL) was first grown at 350 °C, then the temperature was decreased to grow the top layer (TL) at a higher Sn content in the 9–13 at.% range (samples A-D). The other parameters were kept constant during the growth. Figure 1(a) exhibits a typical scanning TEM (STEM) image for sample D with a 50 nm thick TL (13 at.% on a 45 nm-thick BL (4 at.%). Previous structural studies of identical samples confirmed the absence of defects at the GeSn/Ge-VS interface [38], while the two GeSn layers with different compositions and smooth interfaces are visible in the STEM image in figure 1(a). The corresponding RSM map in figure 1(b) shows that the GeSn BL and TL are pseudomorphic with respect to Ge-VS, corresponding to a $r < 5\%$. A similar $r$ was estimated for all samples regardless of the growth temperature. The presence of interference fringes in figure 1(b), also observed in the $2\theta - \omega$ scan around the (004) XRD order, indicates a high degree of crystallinity.

For the relaxed series, 500–700 nm thick GeSn layers were grown at a fixed temperature in the 330 °C–300 °C range, leading to a composition in the 7–13 at.% range (samples E-H). In the TEM image for a 13 at.% Sn layer (figure 1(c)), dislocations are mainly observed within the first 200–300 nm of the GeSn layer [38]. The associated RSM map shows a strong broadening along $q_x$ resulting from plastic relaxation (figure 1(d)) [38], with an estimated $r$ exceeding 75% in all samples (figure 1(e)). The reduced compositional grading at thicknesses above 300 nm leads to a uniform strain and composition profile within the depth probed by Raman measurements. The Sn content for the pseudomorphic and relaxed sets are plotted in figure 1(f) as a function of the growth temperature. An increase in Sn content of 1.3 ± 0.3 at.% for every 10 °C decrease in growth temperature is observed for the pseudomorphic samples, while a higher rate of 2.1 ± 0.2 at.%/–10 °C is estimated for the relaxed layers, resulting from enhanced strain minimization during growth [38, 44]. In addition to the
Table 1. List of samples investigated in this work. The growth temperature $T$, the composition and strain values as estimated from XRD and Raman measurements are shown, as well as parameters extracted from the fits.

| Sample | $T$ (°C) | $y_{XRD}$ (at.% | $y_{Raman}$ (at.% | $\varepsilon_{XRD}$ (%) | $\varepsilon_{Raman}$ (%) | $\omega_{Sn-Sn}$ (cm$^{-1}$) | $\omega_{Ge-Sn}$ (cm$^{-1}$) | $\omega_{DA}$ (cm$^{-1}$) | $\omega_{Ge-Ge}$ (cm$^{-1}$) | $t_{Ge-Ge}$ (cm$^{-1}$) |
|--------|----------|-----------------|-------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| A      | 310      | 8.8             | 9.3               | −1.17          | −1.30          | 182.9          | 260.2          | 290.7          | 299.0          | 1.59           |
| B      | 300      | 10.6            | 10.1              | −1.39          | −1.40          | 181.5          | 259.4          | 291.2          | 298.8          | 1.65           |
| C      | 290      | 12.0            | 11.8              | −1.60          | −1.64          | 180.8          | 258.8          | 291.4          | 298.6          | 1.76           |
| D      | 280      | 13.0            | 13.3              | −1.79          | −1.84          | 179.8          | 258.6          | 291.7          | 298.3          | 1.86           |
| E      | 330      | 6.8             | 7.1               | −0.14          | −0.19          | 181.9          | 256.6          | 288.9          | 295.4          | 1.41           |
| F      | 320      | 8.8             | 8.3               | −0.25          | −0.13          | 179.7          | 255.5          | 288.0          | 294.1          | 1.48           |
| G      | 310      | 10.9            | 11.4              | −0.30          | −0.41          | 178.1          | 254.8          | 287.0          | 292.9          | 1.68           |
| H      | 300      | 13.2            | 13.2              | −0.39          | −0.51          | 176.3          | 254.5          | 286.6          | 291.9          | 1.79           |
| I      | 340      | 4.6             | 4.1               | −0.23          | −0.03          | 183.2          | 259.2          | 289.4          | 297.2          | 1.22           |
| J      | 300      | 13.3            | 13.2              | −0.33          | −0.36          | 175.1          | 254.3          | 286.1          | 291.1          | 1.78           |
| K      | 280      | 15.4            | 16.1              | −1.17          | −1.32          | 175.6          | 254.9          | 287.9          | 293.4          | 2.00           |
| L      | 280      | 16.0            | 16.1              | −1.41          | −1.25          | 175.2          | 254.8          | 287.8          | 293.1          | 2.00           |
| M      | 280      | 16.1            | 17.2              | −1.16          | −1.38          | 175.0          | 254.5          | 287.4          | 292.8          | 2.07           |
| N      | 280      | 16.9            | 14.9              | −1.27          | −0.85          | 173.7          | 254.1          | 287.4          | 292.1          | 1.90           |

- Pseudo-morphic
- Relaxed
- Other
Figure 1. (a), (b) STEM image (a) and RSM around the asymmetrical (224) reflection (b) for the pseudomorphic sample D. (c), (d) TEM image along the [110] zone axis (c) and (224) RSM map (d) for the relaxed sample H. (e), (f) Degree of strain relaxation \( r \) (e) and Sn content (f) as a function of the growth temperature.

pseudomorphic and relaxed sets of samples described above, Raman analysis was extended to six other samples of various values of strain and composition (table 1).

3. Results and discussion

Figure 2(a) and (b) display representative polarized Raman spectra, recorded for sample F (\( y = 8.8 \) at.\%, \( \varepsilon = -0.25 \)\%). For comparison, polarized Raman spectra of a Ge-VS are also displayed in figure 2(c). For both samples, the main Ge-Ge mode (\( \sim 300 \) cm\(^{-1}\)) is much stronger under \( x(z'z')x \) and \( x(zy)x \) configurations as compared to \( x(zz)x \) and \( x(z'y')x \) configurations, which is consistent with the selection rules of LO phonons. For the GeSn layer, the Ge-Sn LO mode (dotted vertical line) shows the same behavior. The shoulder visible on the low wavenumber side of the Ge-Ge peak (dashed vertical line) is related to a DA mode attributed to a maximum in the one-phonon density of states in Ge [15, 45, 46]. Its presence becomes more apparent under the \( x(zz)x \) configuration because of the low intensity of both adjacent LO modes. This additional contribution is accounted for in the fit of the Raman spectra, which provides an accurate identification of the characteristics of each mode. An example of a fitted unpolarized spectrum in the 235–325 cm\(^{-1}\) range is displayed in figure 2(d). The coefficient of determination \( R^2 \) is between 0.9962 and 0.9994 for all samples. In addition, second-order Ge-Ge modes are also detected under the \( x(z'z')x \) and \( x(zz)x \) configurations for the Ge-VS (2TA between 100 cm\(^{-1}\) and 250 cm\(^{-1}\) [16, 47], TO + TA near 350 cm\(^{-1}\) and 2LA near 380 cm\(^{-1}\) [48]). These modes also appear with the same selection rules in the GeSn sample, as well as an additional mode near 180 cm\(^{-1}\) (dash-dotted vertical line). Since this peak does not follow the selection rules of a LO mode, it cannot be straightforwardly assigned to the Sn-Sn mode expected near
The Raman spectra of pseudomorphic and relaxed GeSn samples with variable Sn compositions are displayed in figure 3. Interestingly, as the Sn content increases, the peak positions of the pseudomorphic layers remain almost unaffected by the change in Sn content (figure 3(a)), whereas a progressive shift to lower wavenumbers is observed for both modes for the relaxed layers (figure 3(b)). Due to the relatively larger atomic mass of Sn, when a significant amount of Sn atoms is incorporated into the Ge lattice, a downshift of Ge-Ge and Ge-Sn modes is expected. This behavior is more pronounced in the relaxed layers, whereas it is rather subtle and limited in the pseudomorphic layers. In the latter, the anticipated downshift as a result of Sn incorporation seems to be counterbalanced by the upshift due to the increased compressive strain associated to the higher Sn content in the lattice.

Examples of three-dimensional plots of the Raman shifts $\omega$ (black spheres) for Ge-Ge and Ge-Sn modes as a function of Sn content and strain are shown in figures 4(a) and (b). The measured data points belong to the same planes, which can be described by two-dimensional linear regressions

$$\omega = \omega_0 + ay + b\epsilon,$$

where $\omega_0$ is a characteristic wavenumber, and $a$ and $b$ are the fitting parameters. The linear behavior is expected from phonon deformation potential theory [52]. The resulting fits, superimposed on the scatter plots, and the projections on the 2D space in figures 4(c) and (d) confirm that the linear regressions accurately represent the behavior of the four peaks in all studied samples. The fitting coefficients are listed in table 2 and the errors are calculated considering 95% confidence intervals. $R^2$ being larger than 0.94 and the relatively small errors on both $a$ and $b$ slopes indicate that the planar fits describe adequately the mode distribution. Furthermore, the calculated $\omega_{0,Ge-Ge}$ is equal to the value obtained for bulk Ge and $a$ and $b$ slopes are comparable to those found in earlier studies of the Ge-Ge mode [17, 41]. As for the Ge-Sn mode, $a$ and $b$ values are slightly higher than those of the Ge-Ge mode. However, the slopes of all four peaks are remarkably close and sometimes overlap when considering the uncertainties.

The analysis above demonstrates that the peak positions of the Ge-Ge, Ge-Sn, DA and Sn-Sn like modes evolve qualitatively similarly. The behavior of the integrated intensity, width, and asymmetry of each one of these vibrational modes was also evaluated. We found that an increase in Sn content is associated with an increase in the relative integrated intensity of Ge-Sn and DA modes. The latter also increases as the layers become more compressively strained. Furthermore, we also noticed that the full width at half maximum (FWHM) of both Ge-Ge and Ge-Sn peaks increase with higher Sn content and higher relaxation, as expected from the increase in lattice disorder. As for $t$ of the Ge-Ge peak, included in table 2, it increases with Sn content with a relatively strong correlation ($R^2 = 0.9533$), as shown in figure 4(c). The strain, however, has no measurable impact on $t$ (figure 4(d)). The increasing asymmetry of the Ge-Ge mode due to Sn incorporation is visible in figure 4(c). This explains why the DA peak is less prominent for samples with high Sn contents. The increase of the Ge-Ge peak asymmetry, together with a shift of the peak position to lower wavenumbers, results in a larger superimposition of the two contributions. Nevertheless, this superimposition remains partial and it is still possible to discriminate them, as confirmed by the high $R^2$ obtained in the two-dimensional linear regressions.

Any pair of equations describing peak positions as a function of $y$ and $\epsilon$ would technically be sufficient to estimate the composition and strain of a GeSn layer based on its Raman spectrum. However, since the positions of all modes evolve similarly, this becomes challenging based solely on peak positions. In fact, due to the comparable $a$ and $b$ slopes, the strain...
and composition estimation obtained when solving equations (2) for a pair of peaks will be highly dependent on small changes in the input parameters $\omega$. However, as previously stated, the composition and strain do not only affect the peak positions, but also the peak areas, widths, and asymmetry. For instance, the two-dimensional linear regression of $t_{\text{Ge-Ge}}$ results in $a$ and $b$ coefficients that are very different from those obtained for the peak positions (table 2). Therefore, the composition and strain of GeSn alloys can be extracted directly by solving a set of two equations describing the behavior of the peak position and asymmetry of the main Ge-Ge mode,

$$\omega_{\text{Ge-Ge}} = \omega_{0,\text{Ge-Ge}} + a_{\text{Ge-Ge}} y + b_{\text{Ge-Ge}} \varepsilon,$$

(3)

$$t_{\text{Ge-Ge}} = t_{0,\text{Ge-Ge}} + a_{\text{Ge-Ge}} y + b_{\text{Ge-Ge}} \varepsilon.$$

(4)

This approach allowed to retrieve values which are close to those measured by XRD, as shown in table 1. This is a clear demonstration that combining peak position and asymmetry is sufficient for an accurate analysis of strain and composition in GeSn semiconductors using Raman spectroscopy. To test this approach, we carried out Raman line-scans on under-etched GeSn microdisks [22]. The model enabled the evaluation of the bulk composition with a relative accuracy of 5% in addition to providing the local residual strain across the microdisks, thus clearly demonstrating the relevance of micro Raman spectroscopy to probe the local composition and strain in individual GeSn micro- and nano-structures.

| Regression | $\omega_0$ or $t_0$ (cm$^{-1}$) | $a$ (cm$^{-1}$) | $b$ (cm$^{-1}$) | $R^2$ |
|------------|-------------------------------|----------------|----------------|-------|
| $\omega_{\text{Ge-Ge}}$ | 300.4 ± 0.9 | -84 ± 8 | -491 ± 52 | 0.98 |
| $\omega_{\text{DA}}$ | 291.3 ± 0.7 | -49 ± 7 | -347 ± 45 | 0.97 |
| $\omega_{\text{Ge-Sn}}$ | 261 ± 1 | -68 ± 11 | -347 ± 69 | 0.95 |
| $\omega_{\text{Sn-Sn}}$ | 188 ± 1 | -104 ± 9 | -292 ± 59 | 0.98 |
| $t_{\text{Ge-Ge}}$ | 1.0 ± 0.1 | 6 ± 1 | -5 ± 7 | 0.95 |

4. Conclusion

In summary, we described a detailed investigation of GeSn vibrational modes at variable strain and content. The clear distinction of Raman features was made possible by the use of a 633 nm laser. The broad range of Sn contents of CVD-grown GeSn layers at different relaxation levels allowed the decoupling of the individual effects of composition and strain on the behavior of Raman vibrational modes. We found that the Ge-Ge, Ge-Sn, DA and Sn-Sn like modes all downshift as Sn content increases. Strain relaxation induces qualitatively the same behavior. Exploiting the alloying-induced asymmetry of the
Ge-Ge peak as an additional parameter allowed to simultaneously obtain the strain and Sn content in GeSn layers. These results lay the groundwork to employ Raman spectroscopy for a non-destructive characterization of GeSn-based structures and devices.

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Conflict of interest

The authors declare no competing financial interest.

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