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Temperature dependence of the Raman spectrum in $Ge_{1-y}Sn_y$ and $Ge_{1-x-y}Si_xSn_y$ alloys

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The temperature dependence of the Raman spectrum of Ge-rich $Ge_{1-y}Sn_y$ and $Ge_{1-x-y}Si_xSn_y$ alloys has been determined in the 10- to 400-K range. The Raman line shift and width changes as a function of temperature are found to be virtually identical to those observed in bulk Ge. This result shows that the anharmonic decay process responsible for the temperature dependence is extremely robust against the alloy perturbation, so that the expected relaxation of the wave vector conservation rule does not affect the decay in any noticeable way.

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Group IV, III-V, and II-VI semiconductor alloys are of great interest from a basic physics point of view because, depending on the property under consideration, they lend themselves to an extended state point of view—closely resembling perfect solids—or to a localized description characteristic of disordered systems. Consider, for example, the case of $Si_{1-x}Ge_x$ alloys. The energy eigenvalues for the Si $3s/3p$ states and those for the Ge $4s/4p$ states are very similar, and therefore it is not surprising that the electronic structure can be described in terms of a perfectly periodic "virtual crystal" with an average electronic potential.[1–4] Experimental studies of the dielectric function of the alloys show indeed clear evidence for Van Hove-like singularities, which evolve smoothly, in shape and energy, from Ge to Si,[5,6] even though such singularities are only well defined in the context of perfectly periodic solids. On the other hand, the Raman spectrum of the alloy does not show a single peak evolving from the Raman spectrum of Si to the Raman spectrum of Ge, but three distinct spectral features associated with Si-Si, Si-Ge, and Ge-Ge optical vibrations.[7–9] Such localization effects are not surprising if one takes into account the very large mass difference between Si and Ge. This combination of "localized" phonons with "extended" electronic states gives rise to unique properties, some of which remain unexplained to this day, including the different wavelength dependence of the Raman cross section for each of the alloy Raman features.

The above concept of localized optical vibrations, however, does not convey the full complexity of the alloy vibrational structure. In fact, in many alloy systems, it is possible to define "quasi-dispersion" relations for optical and acoustic phonon branches.[10,11] The approximate validity of this concept in $Si_{1-x}Ge_x$ alloys and similar systems is apparent when one studies the line shape of their Raman modes, which are broader than those in the perfect crystals but much narrower than the Raman bands observed in amorphous materials. This indicates that the crystal momentum conservation rule $\boldsymbol{q}_0 \approx 0$, valid for the wave vector of Raman-active modes in perfect solids, is only partially relaxed in tetrahedral semiconductor alloys. Similarly, phonon confinement effects akin to those observed in single-crystal materials are seen in thin alloy films.[11]

An important vibrational property for which the quasidispersion concept is expected to play an important role is the lifetime broadening of the Raman modes. In perfect Ge and Si crystals, the width of the Raman peak at room temperature and below is essentially determined by the anharmonic decay of the Raman-active phonon of frequency ω_0 into pairs of phonons of frequencies ω_1 and ω_2.[12] Energy conservation requires $\omega_1 + \omega_2 = \omega_0$, and crystal momentum conservation implies $\boldsymbol{q}_1 + \boldsymbol{q}_2 = \boldsymbol{q}_0 \approx 0$. In alloy systems the energy conservation rule remains valid, but the crystal momentum rule could be relaxed. Debernardi *et al.* have used *ab initio* methods to study anharmonic phonon decay in Si and Ge.[13] They find that the many pairs of modes that satisfy the two conservation conditions cluster around frequencies $\omega_1 = 0.35\omega_0$ and $\omega_2 = 0.65\omega_0$, as previously proposed in Ref. 9 to explain the temperature dependence of the Raman linewidths. At these frequencies the phonon density of states for transverse acoustic (TA) and longitudinal acoustic (LA) phonons are quite high, suggesting that a relaxation of the momentum conservation rule by the alloying effect should activate many nearby states, which have the "right" frequencies but the "wrong" wave vectors to participate in the decay. This should result in a stronger temperature dependence of the Raman linewidth. The temperature dependence of the Raman spectrum of $Si_{1-x}Ge_x$ alloys has been studied in detail by Burke and Herman.[14] Quite surprisingly, these authors find that the linewidth of the Si-Si and Ge-Ge modes in the alloy has essentially the same temperature dependence as in bulk Ge and Si. On the other hand, differences in the temperature dependence of the alloy modes relative to the parent semiconductors have been observed by Jiménez and coworkers[15] for the GaAs-like modes in Al-rich $Al_xGa_{1-x}As$ alloys as well as by Verma *et al.* in P-implanted GaAs.[16] These examples suggest that the alloy perturbation might be too weak in $Si_{1-x}Ge_x$ alloys to affect the temperature dependence of the Raman widths. To test this hypothesis, we conducted a study of the temperature dependence of the Ge-Ge mode shifts and widths in $Ge_{1-y}Sn_y$ and $Si_{1-x-y}Ge_xSn_y$ alloys. The lattice mismatch between Ge and α-Sn is 14%, as opposed to 4% in the Si-Ge system, so that Sn represents a much larger perturbation in Ge than Ge in Si. Even stronger disorder is present in the ternary alloy, where Sn atoms coexist with Si atoms. In spite of this enhanced alloy disorder, however, we find that the temperature dependence of the Raman width and shift is the same, within experimental error, as the temperature dependence observed in bulk Ge. These results, combined with the earlier work of Burke and Herman,[14] suggest that anharmonic decay in group-IV alloys is extremely robust against wave vector relaxation effects.

Our Ge$_{1-y}$Sn$_y$ samples were grown using the chemical vapor deposition method introduced by Bauer *et al.*[17] The films are deposited directly on Si using via reactions of Ge$_2$H$_6$ with appropriate amounts of SnD$_4$ at ∼350 °C. Details on the growth procedure can be found in Ref. 18. The ternary Si$_{1-x-y}$Ge$_x$Sn$_y$ alloys were grown by the same method using SnD$_4$, Ge$_2$H$_6$, and Si$_3$H$_8$[19] Raman measurements were performed from 10 K to 450 K in the near-backscattering configuration using the 532-nm laser line of a doubled Nd:YAG laser with excitation power of 25 mW. The samples were mounted strain-free in a closed cycle variable temperature cryostat. The collected scattered light was analyzed using an Acton 500-mm spectrometer and a Si CCD detector.

Figure 1 shows the evolution of the Raman spectrum of a Ge$_{0.98}$Sn$_{0.02}$ sample as a function of temperature. The Raman spectrum of bulk Si, Ge, and α-Sn is well approximated by a Lorentzian line shape. The experimentally observed spectrum is the convolution of this Lorentzian with the instrument's response function, which can be reasonably well described by a Gaussian. The resulting Voigt profile[20] is available as a fitting function in most commercial data analysis software packages, so that the intrinsic widths can be extracted directly from fits with these functions. Alternatively, it has been shown that the intrinsic component of the width is related to the width of the instrument resolution function by[20,21]

$$\Gamma = \Gamma_{\text{exp}} - \frac{\Gamma_G^2}{\Gamma_{\text{exp}}} \qquad (1)$$

where Γ is the intrinsic (approximately Lorentzian in the case of a perfect crystal) full width at half maximum (FWHM), Γ_G the FWHM of the instrument resolution function, and Γ_{exp} the measured FWHM. This formula can then be used to obtain Γ from the measured data without formally fitting with a Voigt profile.

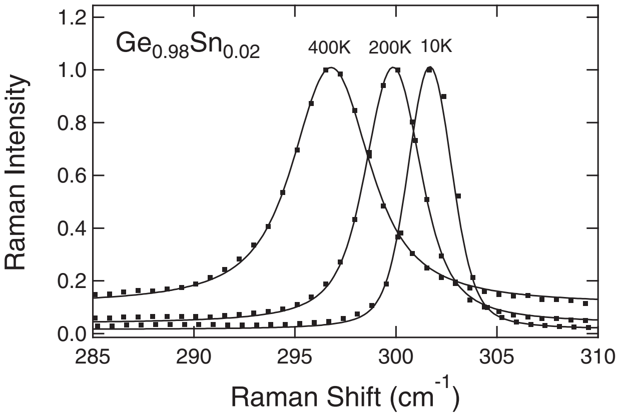

FIG. 1. Raman spectrum of Ge$_{0.98}$Sn$_{0.2}$ obtained with 532-nm excitation at temperatures 10, 200, and 400 K. The scattering configuration was $z\,(x,y)\,\bar{z}$ in Porto notation, where x, y, and z refer to the cubic axes.

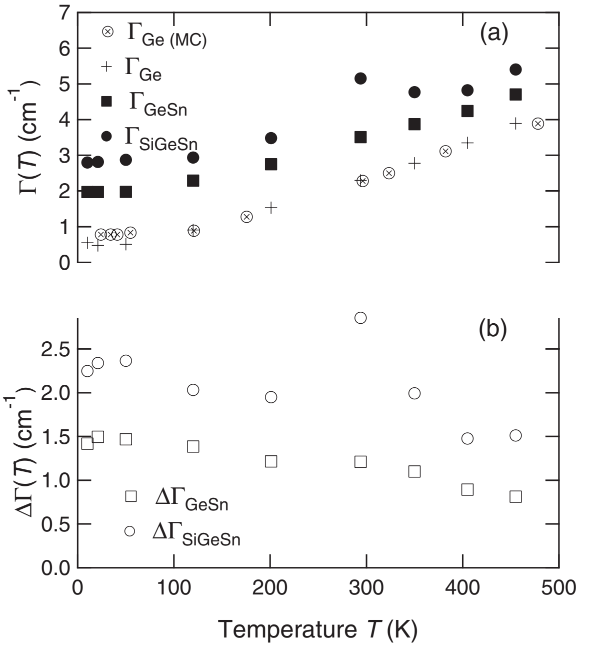

FIG. 2. (a) Linewidths (FWHM) $\Gamma(T)$ of the Ge-Ge mode for Ge (MC, from Ref. 12), Ge (present data), Ge$_{0.98}$Sn$_{0.02}$ and Si$_{0.09}$Ge$_{0.887}$Sn$_{0.023}$ as a function of temperature T. (b) Linewidth difference $\Delta\Gamma(T)$ between Ge$_{0.98}$Sn$_{0.02}$ and Ge and between Si$_{0.09}$Ge$_{0.887}$Sn$_{0.023}$ and Ge.

The analysis of the line shape of alloy modes is much more complicated because, in addition to the lifetime and instrument resolution broadening, there is a broadening contribution from the intrinsic disorder and the relaxation of the wave vector conservation rule. Unfortunately, there are no realistic analytical models that can be used to fit the data and correct for the instrument resolution. Therefore, we adopted the following approximate procedure. We first determine the FWHM of the Raman peaks by fitting with any function that gives good agreement with the data (usually a Voigt profile if the peak looks symmetric or an exponentially modified Gaussian if the peak is asymmetric). Then we assume that we can still use Eq. (1) to correct for the instrumental broadening, even though Eq. (1) has been shown to be valid when the intrinsic line shape is Lorentzian. This approach may introduce a small systematic error, but it will not alter the results in any significant way. In fact, the qualitative conclusions of this Brief Report would not change if we were to ignore instrumental broadening altogether and assume it is part of the intrinsic width. In Fig. 2 we plot the linewidths $\Gamma_{\text{GeSn}}(T)$, $\Gamma_{\text{SiGeSn}}(T)$, and $\Gamma_{\text{Ge}}(T)$ together with the *differences* $\Gamma_{\text{GeSn}}(T) - \Gamma_{\text{Ge}}(T)$ and $\Gamma_{\text{SiGeSn}}(T) - \Gamma_{\text{Ge}}(T)$, where all widths have been obtained following the procedure just described. In Fig. 3 we show the corresponding line shifts $\omega_{\text{GeSn}}(T)$, $\omega_{\text{SiGeSn}}(T)$, and $\omega_{\text{Ge}}(T)$ together with the differences $\omega_{\text{GeSn}}(T) - \omega_{\text{Ge}}(T)$ and $\omega_{\text{SiGeSn}}(T) - \omega_{\text{Ge}}(T)$. We see that all these differences are remarkably constant over the entire range of temperatures studied here. In the case of the linewidth, it has been proposed that the temperature dependence can be fit with an expression of the form[12]

$$\Gamma(T) = \Gamma_0\left[n(\omega_1) + n(\omega_2) + 1\right], \qquad (2)$$

where $n(\omega)$ is the Bose-Einstein expectation number for a phonon of frequency ω. In a rigorous derivation, the anharmonic linewdith is actually a sum of terms of the form Eq. (2), one for each pair of modes with frequencies ω_1 and ω_2 into which the Raman phonon of frequency ω_0 can decay.[22] However, this sum can be replaced by

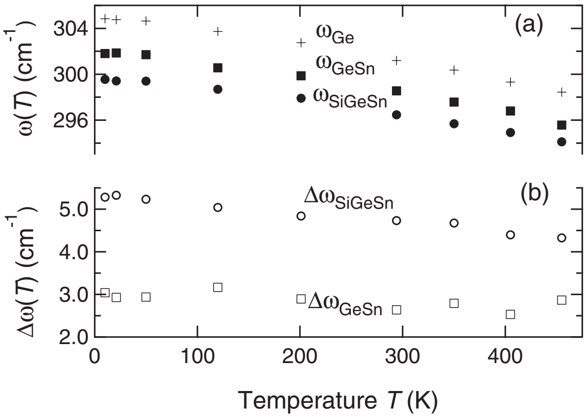

FIG. 3. (a) Peak frequencies $\omega(T)$ of the Ge-Ge Raman mode in Ge, $Ge_{0.98}Sn_{0.02}$, and $Si_{0.09}Ge_{0.887}Sn_{0.023}$ as a function of temperature T. (b) Line shift difference $\Delta\omega(T)$ between $Ge_{0.98}Sn_{0.02}$ and Ge and between $Si_{0.09}Ge_{0.887}Sn_{0.023}$ and Ge.

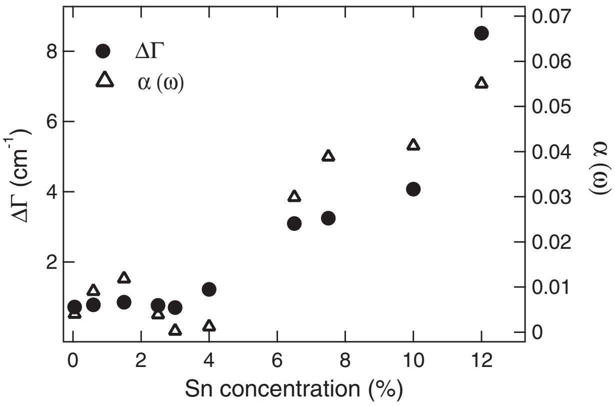

FIG. 4. Circles: compositional dependence of $\Delta\Gamma$ (300 K) for the Ge-Ge mode in $Ge_{1-y}Sn_y$ alloys. Triangles: peak asymmetry indicator α as a function of composition y.

a single term if the possible decay frequencies cluster around a single value, as indicated above for the case of diamond structure semiconductors. Under this simplification the coefficient Γ_0 is proportional to the sum of the squared moduli of the anharmonic matrix elements for each individual decay channel.[12] These matrix elements "contain" the crystal momentum conservation prescription, that is, they vanish if $\boldsymbol{q}_1 + \boldsymbol{q}_2 \neq 0$. In the case of our alloys, we would expect the square bracket in Eq. (2) to remain the same as in bulk Ge, because the two frequencies $\omega_1 = 0.35\omega_0$ and $\omega_2 = 0.65\omega_0$ correspond to regions with high phonon density of states, and the density of states will not be dramatically altered by alloying. However, precisely because the density of states is high, there are many nearby phonon states whose matrix element cancels out due to crystal momentum conservation but should be able to participate in the decay process if this rule is relaxed by alloying. Thus, we might expect an increase in Γ_0 as the main effect of alloying. But the results in Fig. 2 clearly indicate that Γ_0 remains approximately the same as in bulk Ge, thereby contradicting our expectation. Thus the anharmonic decay process appears to be extremely robust against perturbations such as alloying.

The third-order anharmonic line shift is Kramers-Kronig related to the third-order contribution to the linewidth,[22] so we expect the differences $\omega_{\rm GeSn}(T) - \omega_{\rm Ge}(T)$ and $\omega_{\rm SiGeSn}(T) - \omega_{\rm Ge}(T)$ to be constant in view of the results for the linewidth. This is approximately the case from an inspection of Fig. 3. In the case of the $\omega_{\rm SiGeSn}(T) - \omega_{\rm Ge}(T)$ difference, we see a small deviation from the constant shift behavior that can be approximated by a linear T-dependence. This may be due to the fact that thermal expansion and fourth-order terms, unrelated to the third-order perturbation, make a non-negligible contribution to phonon shifts.[12]

The temperature-independent difference between the width of the alloy Raman peaks and those of bulk Ge represent the alloy contribution to the width. This contribution is plotted in Fig. 4. For this plot we chose arbitrarily the value at 300 K, but in view of the lack of temperature dependence, we could have chosen any other temperature. It appears that the broadening is approximately constant for $0 < y < 0.04$, and it grows rapidly for $y > 0.04$. This coincides with the appearance of the typical alloy asymmetries in the line shapes, consisting of a broadening of the low-energy side. One way to quantify this asymmetry is to fit the experimental spectrum with a symmetric line shape $I_{\rm sym}(\omega)$ and define an asymmetry indicator $\alpha(\omega) = [I_{\rm sym}(\omega_0 + \Gamma_{\rm exp}) - I(\omega_0 + \Gamma_{\rm exp})]/I_{\rm sym}(\omega_0 + \Gamma_{\rm exp})$. This function is also shown in Fig. 4. The observation of asymmetric Raman peaks is a clear manifestation of the relaxation of the wave vector conservation rule. Vibrational modes with frequencies close to the bulk Raman mode become Raman active, but since the bulk Raman mode corresponds to the highest frequency optical phonon, all activated modes have lower frequency, thus appearing as a broadening of the low-energy side of the Raman peak.[23] Thus, while clear evidence is seen for a relaxation of the wave vector conservation rule in the Raman scattering process—corresponding to a (electron-mediated) photon-phonon interaction—there is no indication of a similar relaxation for the anharmonic decay process—corresponding to phonon-phonon interactions. Whereas the first of these relaxations can be simulated by computing the Raman spectrum of large supercells with phonons calculated using *ab initio* methods, the latter requires an *ab initio* calculation of the anharmonic decay in large cells. Such calculations, which to the best of our knowledge have never been carried out, would shed light on the surprising temperature dependences reported here.

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