

Composition dependence of the phonon strain shift coefficients of SiGe alloys revisited

J. S. Reparaz,^{a)} A. Bernardi, A. R. Goñi, M. I. Alonso, and M. Garriga
Institut de Ciència de Materials de Barcelona-CSIC, Esfera UAB, 08193 Bellaterra, Spain

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By combining Raman scattering from the cleaved edge and under hydrostatic pressure, we have accurately determined the tetragonal phonon deformation potentials of strained $\text{Si}_{1-x}\text{Ge}_x$ alloys in the entire compositional range for the Ge-like, Si-like, and mixed Si-Ge optical modes. A known biaxial strain is induced on thin alloy layers by pseudomorphic epitaxial growth on silicon and subsequent capping. We also determine the strain shift coefficient of the three modes, which are essentially independent of Ge content between 0.4 and 1. This is key information for an effective use of Raman scattering as strain-characterization tool in SiGe nanostructures. © 2008 American Institute of Physics. [DOI: 10.1063/1.2884526]

A precise knowledge of the phonon deformation potentials (DPs), i.e., the derivative of the optical phonon frequency with respect to an elastic deformation of the lattice, is crucial for an effective use of Raman scattering as powerful strain-characterization tool in compound semiconductor microstructures.¹ In particular, for the SiGe material system, there is a great deal of discrepancy between different literature sources about the exact values of the DPs mainly for intermediate Ge concentrations.²⁻⁷ There might be many reasons for such differences (up to a factor of 2) such as strain relaxation effects for epitaxial layers exceeding the critical thickness,³ the use of polycrystalline samples,⁴ or, as pointed out in Ref. 5, due to large uncertainties in the determination of the phonon frequency for the unstrained alloy as compared with literature data obtained for bulk materials.^{8,9} Such disappointing state-of-the-art is surprising in view of the technological importance of strained SiGe/Si heterostructures and the great potential of Raman scattering to measure built-in strain in nanostructured materials such as superlattices,² self-assembled quantum dots,¹⁰⁻¹³ and complementary metal-oxide semiconductor devices.¹⁴

In practice, for the spectroscopical determination of strain one needs to know the so-called strain shift coefficient, defined as the ratio of the phonon frequency shift over the strain that induces the shift: $b_s = \Delta\omega / \Delta\varepsilon$. For the most frequent case of Raman measurements in backscattering geometry from the (001) surface, the strain is directly determined from the frequency shift of the Raman-allowed *singlet* component of the optical phonons using the expression for the strain shift coefficient given by^{2,6}

$$b_s = \omega_0(-\tilde{K}_{11} \cdot \alpha/2 + \tilde{K}_{12}). \quad (1)$$

Here, ω_0 is the frequency of the unstrained phonon mode, \tilde{K}_{ij} are the dimensionless phonon deformation potentials, as defined in Ref. 1, and $\varepsilon_{\perp} = -\alpha\varepsilon_{\parallel}$ represents the relation between the strain in growth direction and in-plane strain. For the case of a strictly bisotropic stress like in epitaxially grown pseudomorphic layers holds $\alpha = 2C_{12}/C_{11}$, where C_{ij} are the elastic constants of the material. A confusing situation is found in the literature for the accepted values of the strain shift coefficient of the optical phonons in $\text{Si}_{1-x}\text{Ge}_x$ alloys:²⁻⁷

For intermediate Ge concentrations in the range of $0.3 \leq x \leq 0.8$, the values of b_s for the Ge-Ge and the Si-Si mode are twice as large and about 50% higher than for the pure materials, respectively. This is not only counterintuitive but recently appeared theoretical evidence¹⁵ for b_s being fairly constant over the whole concentration range, holding this for the three optical modes of the SiGe alloy.

In order to clarify this inconsistency, we have grown a set of five strained epitaxial SiGe layers on Si with Ge concentrations between 0.1 and 0.75 and measured the shift and splitting of the optical phonons caused by the strain due to the lattice mismatch between alloy and substrate. From these measurements and that of the pressure coefficient of the singlet, we were able to accurately determine two phonon deformation potential constants, \tilde{K}_{11} and \tilde{K}_{12} , as a function of alloy composition. We obtained for the strain shift coefficient of the Ge-Ge, Si-Ge, and Si-Si alloy modes the same flat dependence on Ge content from pure Ge down to $x \sim 0.4$, followed by a slight increase for lower concentrations. Our results are in good qualitative agreement with the calculations of Ref. 15, based on a modified Keating model.

A series of samples containing a strained $\text{Si}_{1-x}\text{Ge}_x$ alloy layer was grown by molecular beam epitaxy on Si(001) substrates at a temperature of 400 °C.¹⁶ The growth sequence consists of deposition of a 100-nm-thick Si buffer layer, followed by the SiGe alloy layer with thickness below critical to ensure pseudomorphism and, finally, a 300 nm-thick Si cap layer. A thick cap layer is crucial to avoid elastic strain relaxation of the SiGe layer after cleavage for micro-Raman measurements from the cleaved edge. The nominal thicknesses of the alloy layers with a Ge concentration $x = 0.73, 0.55, 0.38,$ and 0.26 were 7, 10, 7, and 15 nm, respectively. For these layer thicknesses, we estimate an upper bound of 0.2 cm^{-1} for the frequency shift due to phonon-confinement effects,¹⁷ which is negligible compared to other error sources. For the lowest Ge content of 0.10, a multilayer SiGe/Si structure with a total alloy thickness of 200 nm was deposited to increase the Raman signal without exceeding the critical thickness. The strain and composition of the alloys were determined by x-ray reciprocal space mapping along the (224) diffraction direction and for the lattice constant dependence on composition, we used the relation given elsewhere.^{18,19} All alloys showed good pseudomorphic growth to Si.

^{a)}Electronic mail: sebareparaz@hotmail.com.

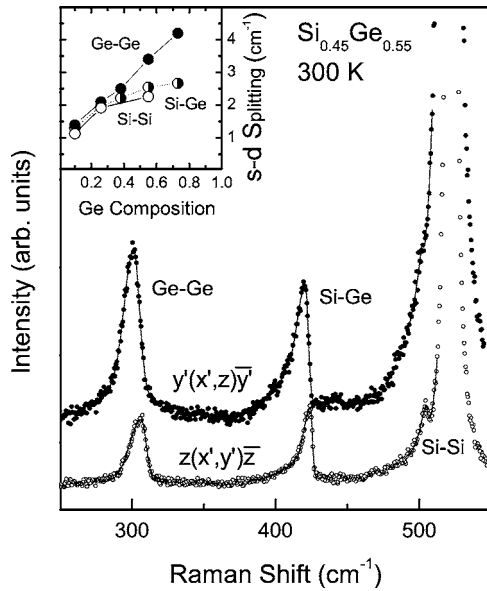


FIG. 1. Representative Raman spectra of a strained alloy layer with Ge content $x=0.55$ measured at room temperature in different scattering configurations with crossed linearly polarized light. Peak assignment to the optical modes of the alloy is indicated. Solid lines represent the results of least-squares fits to the spectra using asymmetric Gaussians. The inset shows the values of the singlet-doublet splitting for the three optical alloy modes as a function of Ge concentration.

Raman spectra were collected in backscattering geometry at room temperature using the 514.5 nm line of an Ar⁺ laser. Raman peak positions are determined with an error of less than 0.5 cm^{-1} . Special care was taken to keep laser power as low as possible to avoid laser heating and the consequent but spurious redshift of the Raman peaks, mainly when exciting at the cleaved edge. A laser power density of 1.5 kW/cm^2 turned out to be adequate. Measurements under pressure were carried out using the diamond anvil cell (DAC) technique. A 4:1 mixture of methanol and ethanol was employed as the pressure-transmitting medium. Pressure was monitored *in situ* by the shift of the Si longitudinal optical phonon. Samples with similar alloy composition but without cap layer were grown for the Raman experiments under pressure. Samples loaded into the DAC were previously thinned to about $30 \text{ }\mu\text{m}$ by mechanical polishing.

The threefold degeneracy of the optical phonon modes at the Brillouin-zone center is lifted at the alloy layer due to the tetragonal distortion of the lattice caused by the bisotropic stress induced by its lattice mismatch to Si. The zone-center phonons split into a singlet (s , vibrations in growth direction) and a doublet (d , in-plane vibrations) component which are apparent in Raman spectra with different linearly polarized light configurations owing to the following selection rules: the singlet component is observed in backscattering from the growth direction using the geometry $z(xy)\bar{z}$, whereas, the doublet component appears in spectra measured in backscattering from the cleaved edge $x'(zy')\bar{x}'$, where x , y , z , x' , and y' are the $[100]$, $[010]$, $[001]$, $[110]$, and $[\bar{1}10]$ crystallographic directions, respectively. Figure 1 shows two representative spectra of the alloy with 0.55 Ge content. Geometries with crossed linear polarization were chosen on purpose in order to suppress contributions from second-order Raman processes by acoustic phonons in Si, which would have hampered the precise determination of the peak position mainly for the Ge-Ge mode. The position of all Raman

peaks was determined by a conventional least-squares fitting procedure using asymmetric Gaussians for the alloy modes and a Lorentzian for the Raman peak of the Si layers. The frequency splitting between peaks measured using both scattering geometries is indicative of a tetragonal strain in the alloy layer. Splitting values of the three alloy modes are plotted as a function of alloy composition in the inset of Fig. 1. The Ge-Ge mode splitting increases linearly with Ge concentration, whereas, for the other modes, the increase of the splitting is sublinear.

The hydrostatic strain-induced shift of the phonon frequencies and the singlet-doublet splitting, which are linear on the strain $\Delta\varepsilon=(a_{\text{Si}}-a_0(x))/a_0(x)$ given by the lattice mismatch, can be written in terms of the adimensional phonon deformation potentials as^{1,20}

$$\frac{\omega_s + 2\omega_d}{3\omega_0} = 1 + \frac{2 - \alpha}{6}(\tilde{K}_{11} + 2\tilde{K}_{12})\Delta\varepsilon, \quad (2)$$

$$\frac{\omega_s - \omega_d}{\omega_0} = -\frac{1 + \alpha}{2}(\tilde{K}_{11} - \tilde{K}_{12})\Delta\varepsilon. \quad (3)$$

Using these equations, one should be able to determine the phonon DPs of the alloys from the measured frequencies of the singlet and doublet components. This method, however, presents a major drawback which concerns large uncertainties derived from the estimation of the unstrained frequency ω_0 from literature data.^{5,8} As an alternative, we propose to get rid of ω_0 by division of Eq. (2) by Eq. (3), adding a third equation which corresponds to the hydrostatic pressure coefficient of the singlet frequency. For that purpose, we have performed Raman measurements using the DAC for every concentration. The logarithmic derivative of the phonon frequency over pressure is readily calculated as:¹³

$$6 \frac{d \ln \omega_s}{dP} = -\frac{\tilde{K}_{11} + 2\tilde{K}_{12}}{B_0^{\text{SiGe}}} + (2\tilde{K}_{12} - \alpha\tilde{K}_{11}) \left(\frac{1}{B_0^{\text{SiGe}}} - \frac{1}{B_0^{\text{Si}}} \right), \quad (4)$$

where B_0 is the bulk modulus of the corresponding material. For the alloys, B_0 was obtained by linear interpolation between the values of the pure elements. The second term in Eq. (4) represents the correction to the phonon pressure coefficient due to the different elastic properties of alloy and Si substrate, which tends to reduce the lattice mismatch strain with increasing pressure. This correction amounts up to 15% for high Ge concentrations, hence, it has to be taken into account for an accurate determination of the phonon DPs. The key point is that ω_0 does not appear explicitly in Eq. (4).

We obtain a system of two linear equations with two unknowns, which is easily solved to obtain the phonon deformation potentials \tilde{K}_{11} and \tilde{K}_{12} plotted in Fig. 2 as a function of Ge concentration for the three optical modes of the SiGe alloy. The values corresponding to the pure materials are the ones tabulated in Ref. 1, but for Ge, they were increased in absolute value by 13.5% in order to account for the correct Grüneisen parameter $\gamma=(\tilde{K}_{11}+2\tilde{K}_{12})/6$ obtained from hydrostatic pressure experiments.²¹ As already performed for GaAs (Ref. 22) and Si,²³ such a correction is necessary because of a systematic underestimation of the applied stress due to surface strain relaxation in the uniaxial-stress Raman experiments performed with a laser energy above the band gap of the material. Despite the relatively large error bars for Si rich alloys, the overall picture that

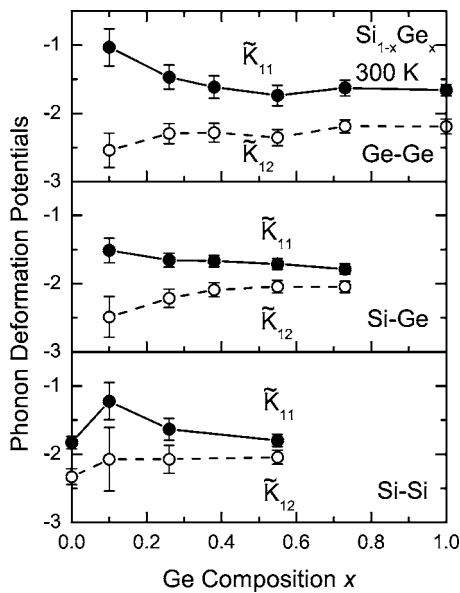


FIG. 2. Dependence on Ge concentration of the phonon deformation potentials \tilde{K}_{11} and \tilde{K}_{12} of the Ge-Ge, Si-Ge, and Si-Si optical modes for the SiGe material system. Solid lines are guides for the eyes.

comes out of Fig. 2 is that both deformation potentials for all SiGe alloy modes are essentially constant, exhibiting \tilde{K}_{11} and \tilde{K}_{12} , a slight tendency to decrease or increase in absolute value with decreasing Ge content, respectively.

Using Eq. (2) and the values for the DPs of Fig. 2, one can calculate ω_0 , and hence, the strain shift coefficient b_s for all phonon modes of the alloy. The resulting values are plotted in Fig. 3 as a function of the composition of the SiGe alloy. The curves represent the results of a least-squares fit to the experimental data using for all modes the same phenomenological expression given by $b_s = b_4(x-1)^4 + b_0$, where x is the Ge content and b_4 and b_0 are adjustable parameters. Interestingly, $b_4 = -190(15) \text{ cm}^{-1}$ has a common value for all three optical modes, whereas, b_0 are $-460(20) \text{ cm}^{-1}$, $-555(15) \text{ cm}^{-1}$, and $-650(20) \text{ cm}^{-1}$ for the Ge-Ge, Si-Ge, and Si-Si phonon mode, respectively. Numbers in parenthesis are the corresponding error bars. These values are in good

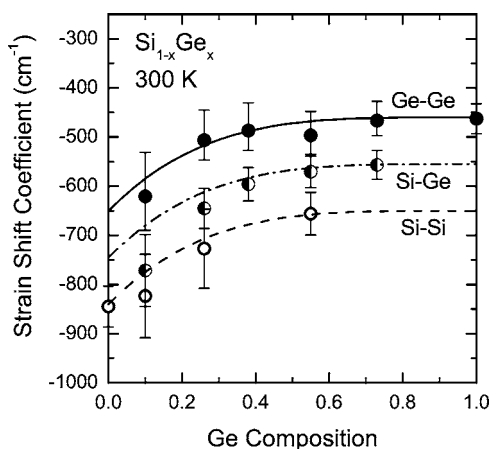


FIG. 3. Phonon strain shift coefficient b_s of the Ge-Ge, Si-Ge, and Si-Si optical modes of $\text{Si}_{1-x}\text{Ge}_x$ alloys as a function of composition. The curves represent the results of a fit to the data points using the same phenomenological polynomial function.

agreement with the ones obtained by Volodin *et al.*⁹ for high Ge content.

A comparison between our b_s values and the collection of data in Fig. 3 of Ref. 15 suggests a much better agreement with the calculations within the modified Keating model, which predict constant strain shift coefficients. This settles the issue about the discrepancies between the different experimental and theoretical reports of the literature. The main conclusion is that the strain shift coefficients of the Ge-Ge and Si-Si modes, to a good approximation, depend only slightly on composition. The strain shift coefficient of the Si-Ge mode is just the arithmetic average of the coefficients of the other two modes. Thus, the results of Fig. 3 are of great practical importance for they provide accurate values for the strain shift coefficient of the optical phonons of $\text{Si}_{1-x}\text{Ge}_x$ alloys to be used for the proper determination of the strain status of SiGe nanostructures by Raman scattering.

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