PHYSICAL REVIEW B VOLUME 54, NUMBER 18 1 NOVEMBER 1996-II

Carbon dependence of Raman mode frequencies in $Si_{1-x-y}Ge_xC_y$ alloys

M. Meléndez-Lira,* J. Menéndez, W. Windl, O. F. Sankey, G. S. Spencer, S. Sego, and R. B. Culbertson
Department of Physics and Astronomy, Arizona State University, Tempe, Arizona 85287-1504

A. E. Bair and T. L. Alford
Department of Chemical, Bio, and Materials Engineering, Arizona State University, Tempe, Arizona 85287-6006

(Received 1 July 1996)

The frequencies of the Si-Si, Si-Ge, and Ge-Ge Raman modes in $Si_{1-x-y}Ge_xC_y$ alloys with $y \leqslant 0.03$ have been measured. All frequencies are found to increase as a function of the carbon concentration. Within experimental error, this dependence is linear with a large slope, which can be explained qualitatively in terms of the large bond distortions caused by the lattice mismatch between $Si_{1-x}Ge_x$ and diamond. Good numerical agreement with theoretical predictions is obtained if the mode frequencies are plotted as a function of the substitutional carbon fraction determined from Rutherford backscattering studies. For the ''Si-Si'' mode, the magnitude of the carbon contribution to the bond-distortion dependence of the Raman frequency shift is found to be 15 times larger than the Ge contribution. This disagrees with the 8-to-1 strain compensation ratio predicted form Vegard's law, but agrees well with theoretical predictions of this ratio. [S0163-1829(96)04742-X]

I. INTRODUCTION

The recent fabrication of $Si_{1-x-y}Ge_xC_y$ alloys has attracted considerable interest. While the bulk solubility of C in Si is limited to the 10^{17}-cm^{-3} range,[1] layers with up to 3% of C have been grown using a variety of nonequilibrium techniques, such as chemical vapor deposition (CVD), molecular-beam epitaxy (MBE), and ion implantation.[2–12] The availability of excellent quality layers with an equilibrium lattice constant *smaller* than that of Si opens up additional band-engineering options in the technologically important Si-Ge arena.

The predicted structural and electronic properties of $Si_{1-x-y}Ge_xC_y$ alloys are very unusual. The calculated equilibrium lattice constant[13–15] deviates considerably from a linear interpolation between the lattice constants of the parent semiconductors (Vegard's law[16]). Electronic structure calculations[17–19] find the band gap to decrease as a function of the carbon concentration y for $y \leqslant 0.1$, even though the band gaps of diamond (5.7 eV) and cubic SiC (2.2 eV) are much larger than the band gap of Si (1.1 eV). Recent vibrational studies indicate that the eigenmode frequencies depend strongly on the microscopic carbon distribution.[20]

In this paper, we report a detailed study of the carbon-concentration dependence of the Si-Si, Ge-Ge, and Si-Ge Raman-active modes in $Si_{1-x-y}Ge_xC_y$ alloys. A previous preliminary study[21] suggested that the Si-Si bonds do not return to their natural length in pure Si when the C fraction compensates for the Ge-induced epitaxial strain. This conclusion is reexamined here in the light of recent advances in the characterization of these alloys as well as in their theoretical understanding.

The compositional dependence of Raman-active modes in alloy semiconductors is sensitive to the local microscopic structure, since the frequencies of optical modes are mainly determined by nearest-neighbor force constants. Information on the local atomic structure can also be obtained from extended x-ray-absorption fine-structure (EXAFS) measurements, but results from this technique are quite controversial for the $Si_{1-x}Ge_x$ system. Large discrepancies among experiments[22–25] and between experiment and theory[26–29] have been found for nearest-neighbor bond lengths. Interestingly, the calculated[30] frequencies of the Raman-active optical modes in $Si_{1-x}Ge_x$ are in excellent agreement with experiment, indirectly supporting the theoretical bond length predictions. Since the presence of carbon in the $Si_{1-x-y}Ge_xC_y$ lattice induces very large local bond distortions, the carbon dependence of Raman frequencies represents a crucial test of theory. Within experimental uncertainties to be discussed below, we find that our data are in good agreement with predictions by Rücker and Methfessel.[31] Moreover, a consistent picture of the Ge dependence and C dependence of the mode frequencies is obtained when the theoretical lattice constant predictions (which disagree with Vegard's law) are taken into account.

Our paper is organized as follows: in Sec II, we discuss the growth and characterization of our $Si_{1-x-y}Ge_xC_y$ films and the procedure utilized to extract the carbon dependence of the vibrational frequencies from the experimental data. In Sec. III we discuss our results in detail and compare with theory. Final conclusions are presented in Sec. IV.

II. METHODS

A. Sample preparation and characterization

Our samples were grown at Lawrence Semiconductor Research Laboratory Inc., by atmospheric-pressure CVD on Si(100) substrates. SiH_2Cl_2 was used as a Si source, GeH_4 as a Ge source, and C_2H_2 as a carbon source. The samples were characterized using Rutherford backscattering spectroscopy (RBS) and x-ray diffraction. For the Raman work we considered only fully strained films with excellent crystallinity,

TABLE I. Structural parameters of the $Si_{1-x-y}Ge_xC_y$CVD-grown thin films studied. χ_{min} is obtained from Rutherford backscattering spectroscopy. $y(y_{sub})$ is the total (substitutional) carbon as obtained from Rutherford backscattering spectroscopy.

SAMPLE	Ge content x	Total carbon y	Substitutional carbon y_{sub}	$a_{\parallel}$ (Å)	$a_{\perp}$ (Å)	χ_{min}	Thickness (Å)
9J	0.22	0.01	0.0057	5.432	5.495	0.04	1200
12C	0.21	0.013	0.007	5.431	5.491	0.046	2250
12L	0.21	0.01	0.0054	5.431	5.491	0.048	5700
13A	0.21	0.0095	0.0043	5.432	5.496	0.036	1250
13N	0.22	0.01	0.003	5.432	5.495	0.058	3500
14C	0.495	0.034	0.018	5.432	5.559	0.10	610
14D	0.495	0.030	0.014	5.433	5.573	0.09	610
18S	0.18	0.009	0.0048	5.432	5.479	0.04	7600

as evidenced by RBS χ_{min} parameters of 0.1 or better. Table I summarizes the parameters of the samples selected for the Raman work.

The frequency of Raman modes in epitaxial alloy semiconductors depends on the composition of the alloy and on the epitaxial strain. Since the presence of carbon has a large effect on the epitaxial strain, it is necessary to quantify this effect in order to extract the intrinsic carbon dependence of the mode frequencies in bulk, unstrained alloys. We performed high-resolution x-ray measurements of $a_{\parallel}$ and $a_{\perp}$, the lattice constants of our films parallel and perpendicular to the growth plane. The lattice constant of the corresponding unstrained alloy is obtained from a straightforward application of elasticity theory. This requires the elastic constants of $Si_{1-x-y}Ge_xC_y$, which we assume to be the same as those of $Si_{1-x}Ge_x$ with the same Ge fraction x. We expect this to be a good approximation for small carbon concentrations. The elastic constants of $Si_{1-x}Ge_x$ are obtained by linear interpolation between those of Si and Ge.

B. Carbon concentration

The x-ray measurements described above can also be used to determine the carbon concentration if the compositional dependence of the lattice constant is known. In the past, carbon concentrations have been extracted from x-ray data under the assumption that the $Si_{1-x-y}Ge_xC_y$ system follows Vegard's law. Recently, however, large deviations from Vegard's law have been predicted on the basis of empirical as well as *ab initio* calculations.[13–15] These results cast serious doubts on the reliability of the x-ray method for the determination of carbon concentrations. Infrared absorption by the Si-C vibrational mode at 605 cm^{-1} has been used to determine the substitutional carbon concentration in Czochralski-grown Si,[1] but the absorbance of the local mode has only been calibrated up to concentrations of the order of 1 ppm. The Si-C mode is also Raman active, suggesting that its Raman intensity could be used to determine the carbon concentration. In fact, Raman scattering offers the advantage over infrared absorption that no absolute intensity measurements are required. This is because one can compare the intensity of the Si-C Raman peak at 605 cm^{-1} with the intensity of the Si-Si peak near 500 cm^{-1}. (The Si-Si mode is infrared forbidden, which explains why the Raman method cannot be duplicated with infrared-absorption measurements.) Unfortunately, however, the polarizabilities of the Si-Si and Si-C bonds are expected to be different, so that the relative intensities of Raman peaks associated with stretching motions of these bonds are not directly proportional to their relative abundances. We find that RBS measurements using the 4.265-MeV $^{12}C(^4He,^4He)^{12}C$ resonance is the most reliable method for the determination of the carbon concentration. We also use RBS spectra from 2-MeV $^4He^{++}$ ions to measure the Ge concentration. In the case of carbon-free $Si_{1-x}Ge_x$ alloys, Ge concentrations obtained from RBS are in excellent agreement with Raman measurements using the known compositional dependence of the Si-Si Raman frequency in this system.

RBS measurements for random sample orientations yield the *total* carbon concentration in our films. The location of this carbon in substitutional sites can be monitored with RBS channeling studies. Using this technique, Sego, Bair, and Alford[32] found recently that only a fraction of the order of 50% of the total carbon concentration can be confirmed to occupy substitutional sites. In the remainder of this paper, we will indicate the substitutional carbon concentration determined from channeling experiments as y_{sub}. The symbol y is reserved for the total carbon concentration. The remainder of the carbon is referred to as ''nonsubstitutional carbon.'' However, it is important to emphasize that the channeling results are consistent with the remaining carbon being tetrahedrally bound to the Si and Ge atoms, while generating large local bond distortions.

In our $Si_{1-x-y}Ge_xC_y$ films grown by CVD, the measured lattice constant seems to follow Vegard's law when plotted as a function of y_{sub}.[32] This finding suggest that nonsubstitutional carbon increases the lattice constant, since the calculated lattice constant values for 100% substitutional carbon are substantially smaller than the predictions from Vegard's law.[13,15] If the experimental findings for CVD-grown films are corroborated in samples grown by other methods, the results of Sego, Bair, and Alford[32] suggest that x-ray measurements based on Vegard's law may in fact yield the correct substitutional carbon fraction due to what appears to be an accidental cancellation of effects between substitutional and nonsubstitutional carbon.

Theoretical predictions of lattice-dynamical properties of $Si_{1-x-y}Ge_xC_y$ alloys assume 100% substitutional carbon.[31]

This implies that the compositional dependence of Raman modes obtained from our samples cannot be compared directly with theory. However, an intriguing agreement with the theoretical predictions is found under the assumption that the Raman frequencies depend on nonsubstitutional carbon only through its effect on the lattice constant of the alloy. This is discussed in detail in Secs. III and IV.

C. Determination of Raman shifts

The Raman experiments were performed at room temperature in the perfect backscattering $z(x,y)\overline{z}$ configuration; x, y, and z correspond to the [100], [010], and [001] crystal directions. The 4880-Å line from an Ar^+ laser was used, and a Spex 1404 double monochromator equipped with a CCD (charge coupled device) detector was employed to analyze the scattered light. Since the amount of carbon that can be incorporated into $\mathrm{Si}_{1-x-y}\mathrm{Ge}_x\mathrm{C}_y$ films is small, the carbon dependence of the phonon frequencies can only be extracted if the Ge concentration and the epitaxial strain are known with great accuracy. In principle, composition-related errors could be reduced by performing experiments on the binary compounds $\mathrm{Ge}_{1-y}\mathrm{C}_y$ and $\mathrm{Si}_{1-y}\mathrm{C}_y$. In these cases, however, the Raman modes of the films would overlap the Raman modes of the substrate materials Ge and Si. Our experience with $\mathrm{Si}_{1-y}\mathrm{C}_y$ films shows that this overlap introduces large systematic errors in the measured compositional dependence of the Si-Si mode. On the other hand, the Si-Si mode in $\mathrm{Si}_{1-x-y}\mathrm{Ge}_x\mathrm{C}_y$ is shifted from the Si-Raman mode in the substrate by the combined effect of Ge and C. If the Ge contribution can be subtracted, one can determine the frequency shifts due to carbon while avoiding an overlap between the Si-Si mode of the film and the Raman mode of the Si substrate. This is the approach followed here.

The compositional dependence of phonon modes in $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloys has been the subject of several experimental studies,[33–37] but the discrepancies among different authors are still significant. This is in part due to errors in the measurement of the compositional fraction x. There is also evidence that compositional fluctuations may affect the frequencies of some of the Raman-active modes.[36] In materials grown by epitaxial techniques such as MBE, several authors have found evidence of spontaneous ordering,[38] which may also affect phonon frequencies.

The best-known compositional dependence of Raman frequencies in $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloys is that of the Si-Si mode in Si-rich alloys. Results from Refs. 33–37 are very well explained by assuming a room-temperature linear dependence given by $\omega_{\text{Si-Si}}=520-68x$ (in cm^{-1}). The other major features in the Raman spectrum of $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloys are the Si-Ge peak and the Ge-Ge peak. Uncertainties in the compositional dependence of these modes are larger. For the Si-Ge mode in $x<0.5$ alloys, Tsang *et al.*[37] proposed $\omega_{\text{Si-Ge}}=400.5+14.2x$ (in cm^{-1}). For the Ge-Ge mode in Si-rich alloys, these authors proposed $\omega_{\text{Ge-Ge}}=282.5+16x$ (in cm^{-1}).

The epitaxial strain dependence of phonon frequencies has also been the subject of several papers.[36,37,39,40] The strain-shifted frequencies can be computed from the measured phonon deformation potentials in bulk samples under stress. Some complications arise from the fact that the measured Raman phonon deformation potentials appear to depend on the laser wavelength used.[41] This is presumably related to the penetration depth of the light. Measurements with infrared excitation are probably more reliable due to the longer penetration depth. An additional complication is the report by Lockwood and Baribeau of a strong compositional dependence of the phonon deformation potentials.[40] For the Si-Si mode in epitaxial $\mathrm{Si}_{1-x}\mathrm{Ge}_x$/Si alloys, however, we find that all data in the literature can be satisfactorily explained by assuming composition-independent phonon deformation potentials. The best fit to the epitaxial strain shifts is $\Delta\omega_{\text{Si-Si}}=-830\varepsilon_{\parallel}(x)$, where $\varepsilon_{\parallel}(x)=[a(\mathrm{Si})-a(\mathrm{Si}_{1-x}\mathrm{Ge}_x)]/a(\mathrm{Si}_{1-x}\mathrm{Ge}_x)$. This is in very good agreement with Raman measurements in bulk Si under stress using infrared laser excitation.[41] For Si-Ge and Ge-Ge modes, Tsang *et al.*[37] proposed $\Delta\omega_{\text{Si-Ge}}=-575\varepsilon_{\parallel}(x)$ and $\Delta\omega_{\text{Ge-Ge}}=-384\varepsilon_{\parallel}(x)$, respectively. We write the compositional dependence of the Si-Si mode in $\mathrm{Si}_{1-x-y}\mathrm{Ge}_x\mathrm{C}_y$ alloys as

$$\omega_{\text{Si-Si}}(x,y)=520-68x+\Delta\omega_{\text{Si-Si}}(y)-830\varepsilon_{\parallel}(x,y), \quad (1)$$

where $\Delta\omega(y)$ is the compositional dependence of this mode in bulk, strain-free $\mathrm{Si}_{1-y}\mathrm{C}_y$ alloys. Since $\varepsilon_{\parallel}(x,y)=\varepsilon_{\parallel}(x)+\varepsilon_{\parallel}(y)$ to first order, Eq. (1) contains all contributions to $\omega_{\text{Si-Si}}(x,y)$ to first order in x and y. The Ge dependence of the ''Si-Si'' mode is known from experiment to be linear. A linear approximation should also be reasonable for the y dependence given the small carbon concentrations in our samples. This will be further discussed in Sec. IV. Equation (1) also assumes that the coefficient of the epitaxial strain term is not only independent of the germanium concentration, as discussed above for the case of $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloys, but also independent of the carbon concentration.

Similarly, we use the following linear expressions for the compositional dependence of the Si-Ge and Ge-Ge modes:

$$\omega_{\text{Si-Ge}}(x,y)=400.5+14.2x+\Delta\omega_{\text{Si-Ge}}(y)-575\varepsilon_{\parallel}(x,y), \quad (2)$$

$$\omega_{\text{Ge-Ge}}(x,y)=282.5+16x+\Delta\omega_{\text{Ge-Ge}}(y)-384\varepsilon_{\parallel}(x,y). \quad (3)$$

The carbon dependence $\Delta\omega(y)$ for the three main Raman modes is obtained by combining our experimental data with Eqs. (1), (2), and (3). For this purpose we use the Ge fraction x determined from the RBS measurements, and the epitaxial strain $\varepsilon_{\parallel}$ obtained from the x-ray measurements.

III. RESULTS

Figures 1 and 2 show representative Raman spectra from $\mathrm{Si}_{1-x-y}\mathrm{Ge}_x\mathrm{C}_y$ samples with different amounts of Ge and C. The spectra show the familiar Ge-Ge, Si-Ge, and Si-Si structures observed in $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloys. In addition, we observe additional Raman features near 605 cm^{-1}, assigned to Si-C vibrations, and near 560 cm^{-1}, which can be assigned either to a Ge-C mode or to a Si-C mode with two carbon atoms as second neighbors.[20] We have not observed a systematic frequency shift of these additional modes as a function of the carbon concentration. A detailed study will be published elsewhere.[42]

The spectra in Figs. 1 and 2 also show the Raman peak of the Si substrate. This peak is used as a reference to determine the frequency shifts in the alloy. The carbon dependence of

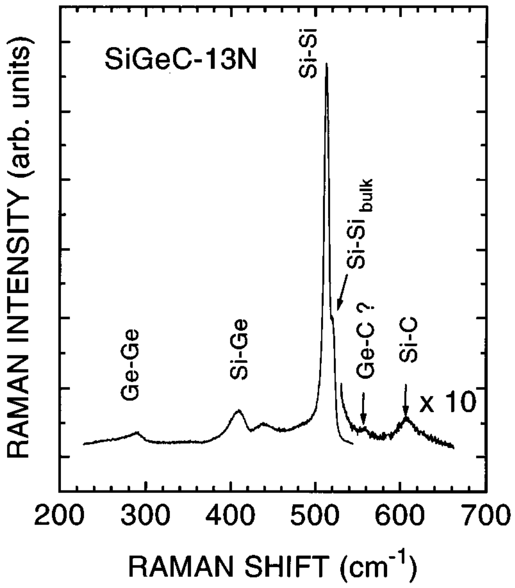

FIG. 1. Raman spectrum of a $Si_{0.77}Ge_{0.22}C_{0.01}$/Si thin film. In addition to the Raman modes associated with the alloy, the Raman signal from the substrate is clearly seen at 520 cm^{-1}.

the Si-Si, Si-Ge, and Ge-Ge modes is obtained following the procedure discussed in Sec. II. The resulting dependences, i.e., the function $\Delta\omega(y)$ in Eqs. (1–3), are plotted in Fig. 3. We have arbitrarily chosen to plot this dependence as a function of y_{sub}. A similar plot, with a slope reduced by a factor of the order of 2, would be obtained if we express the frequency shifts as a function of the *total* carbon concentration y.

The results in Fig. 3 are fit with a linear expression of the form $\Delta\omega(y_{sub})=Ay_{sub}+B$. The coefficient B is expected to be zero, but is kept in the fit as a way to minimize systematic errors arising from our determination of the Ge concentration and from the assumed compositional dependence of the modes in $Si_{1-x}Ge_x$ alloys. Hence the linear term Ay_{sub} represents the compositional dependence of the three main peaks as a function of the carbon concentration. Using our measured values x, y, y_{sub}, $\Delta\omega$, and $\varepsilon_{\parallel}$, we obtain

$$\Delta\omega_{Si\text{-}Si}(y)=(190\pm40)y_{sub}(cm^{-1}), \tag{4}$$

$$\Delta\omega_{Si\text{-}Ge}(y)=(320\pm43)y_{sub}(cm^{-1}), \tag{5}$$

$$\Delta\omega_{Ge\text{-}Ge}(y)=(370\pm125)y_{sub}(cm^{-1}). \tag{6}$$

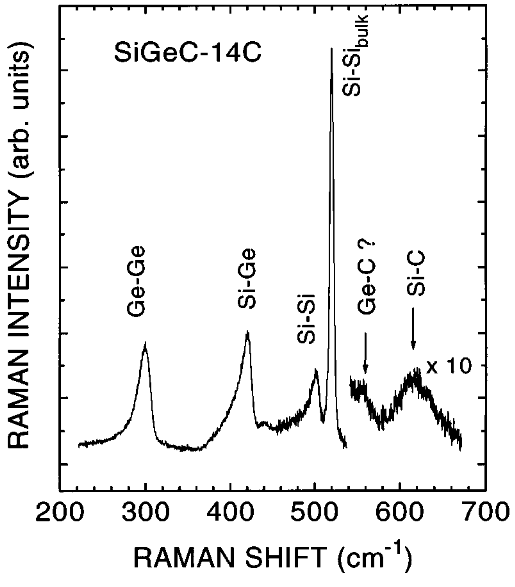

FIG. 2. Raman spectrum of a $Si_{0.47}Ge_{0.495}C_{0.034}$/Si thin film. Notice that the substrate peak is much more prominent here than in Fig. 1. This is due to the smaller thickness of this sample.

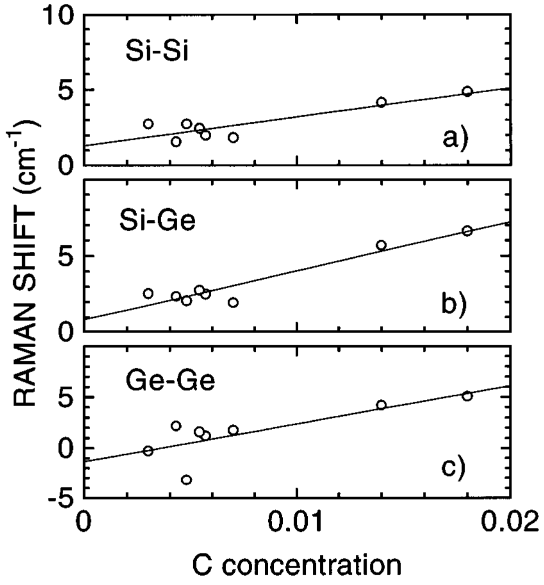

FIG. 3. Carbon dependence $\Delta\omega(y)$ of the Raman frequency plotted as a function of the substitutional carbon concentration y_{sub} for (a) Si-Si modes, (b) Si-Ge modes, and (c) Ge-Ge modes in $Si_{1-x-y}Ge_xC_y$. The lines represent a linear fit, as discussed in the text.

The uncertainty corresponds to the standard deviation as obtained from the linear fitting. In addition to the accidental error quoted in Eqs. (4)–(6), it is important to stress again that these compositional dependences are based on the validity of Eqs. (1)–(3), which assume the additivity of the Ge and C dependences of the mode frequencies.

IV. DISCUSSION

The carbon dependence of the Raman mode frequencies shown in Eqs. (4)–(6) is much stronger than the dependence of the same modes on the Ge fraction. As discussed above, systematic errors due to the Ge dependence of the Raman frequencies are likely to be much larger for the Ge-Ge and Si-Ge modes. Hence we concentrate here on the compositional dependence of the Si-Si mode. Even for this mode, however, we face an uncertainty of a factor of up to 2 in the linear coefficient of the carbon dependence, since the decision to plot the frequency shift as a function of the substitutional carbon fraction is rather arbitrary. Within the context of Eq. (1), this choice is equivalent to assuming that nonsubstitutional carbon only affects the mode frequencies through its effect on the lattice constant, which might be the case if the Si-Si mode eigenvectors had very small amplitude in those regions of the sample where nonsubstitutional carbon is located. This cannot be verified until the nature and location of nonsubstitutional carbon is well established. Interestingly, however, the compositional dependence of the Si-Si mode derived from Eq. (1) is in very good agreement with the theoretical prediction from Rücker and Methfessel $\Delta\omega_{\text{Si-Si}}(y)=210y$ for $\text{Si}_{1-y}\text{C}_y$ alloys in which C is fully substitutional.[31] These authors use an extended Keating model fit to *ab initio* results for Si, Ge, C, SiC, SiGe, and GeC. The model gives excellent agreement with the known compositional dependence of Raman modes in $\text{Si}_{1-x}\text{Ge}_x$ alloys.

The sign and large magnitude of the C dependence of the Si-Si mode frequency can be understood in terms of ideas advanced earlier to explain the compositional dependence of modes in $A_{1-x}B_x$ group-IV alloys.[21,31,43,44] As indicated above for the case of the $\text{Si}_{1-x}\text{Ge}_x$ system, the Raman spectra from these alloys are dominated by three main structures, informally referred to as A-A, B-B, and A-B peaks. Due to the large mass difference between the A and B atoms, the B atoms are not expected to participate in A-A-type vibrations. Realistic calculations show this to be an excellent approximation when the A atom is the lighter one. The approximation remains reasonable even in cases when the optical branches of A overlap the acoustic branches of B. Hence the effect of mass disorder on the frequency of optical modes is closely related to the phonon confinement shifts in short-period superlattices and small particles.[45] Confinement *lowers* the phonon frequency when the phonon branches have a negative dispersion, i.e., when the zone-center optical phonon is the highest-frequency vibration in the crystal.

A second contribution to the phonon energy shift as a function of composition arises from the mismatch between the A and B lattices. This mismatch is accomodated by local changes in bond lengths and angles, which induce shifts in the phonon frequencies. The sign of the frequency shifts depends on the nature of this microscopic strain. *Compressive* strain usually increases the Raman frequency, whereas *tensile* strain shifts the peaks to lower frequency. When these alloys are grown epitaxially on a substrate, there is an *additional* contribution to the Raman frequency shift which depends on the mismatch strain. This contribution is given by the last term in Eqs. (1)–(3).

The added effects of mass disorder and microscopic strain determine the sign and magnitude of the compositional dependence of Raman modes in bulk $A_{1-x}B_x$, group-IV alloys. When the microscopic strain is tensile, the two contributions tend to reduce the mode frequency. This is the case for the Si-Si mode in $\text{Si}_{1-x}\text{Ge}_x$ alloys. On the other hand, when the microscopic strain is compressive, the two contributions have opposite sign. This is the case for the Ge-Ge mode in $\text{Si}_{1-x}\text{Ge}_x$ and the Si-Si mode in $\text{Si}_{1-y}\text{C}_y$. We note, however, that the Ge-Ge frequency *decreases* as a function of the Si fraction in $\text{Si}_{1-x}\text{Ge}_x$ alloys, whereas here we find that the Si-Si frequency *increases* as a function of the C concentration in $\text{Si}_{1-y}\text{C}_y$ alloys. The lowering of the Ge-Ge frequency as a function of the Si concentration in $\text{Si}_{1-x}\text{Ge}_x$ alloys indicates that the mass disorder contribution to the frequency shift is larger than the microscopic strain term. This situation is found to be reversed in $\text{Si}_{1-y}\text{C}_y$ alloys, because the lattice mismatch between Si and diamond is eight times larger than the one between Si and Ge. Hence our finding of a rapidly increasing mode frequency as a function of the carbon concentration is explained in terms of a large microscopic strain contribution. This conclusion is valid not only for the Si-Si mode but also for the Si-Ge and Ge-Ge modes, whose frequencies also increase rapidly as a function of the carbon concentration.

TABLE II. Mass disorder and microscopic strain contributions to the compositional dependence of Raman mode frequencies in group-IV alloys. The mass disorder effect is computed as discussed in the text. The microscopic strain contribution is simply the difference between the experimental dependence and the computed mass disorder contribution.

Mode	Experiment	Mass disorder contribution (cm^{-1})	Microscopic strain contribution (cm^{-1})
Si-Si in $\text{Si}_{1-y}\text{C}_y$	$190y$[a]	$-77y$	$+267y$
Si-Si in $\text{Si}_{1-x}\text{Ge}_x$	$-68x$[b]	$-49x$	$-19x$
Ge-Ge in $\text{Si}_{1-x}\text{Ge}_x$	$-16x$[c]	$-33.3x$	$+17.3x$

[a] This work.
[b] From Ref. 35.
[c] From Ref. 37.

Further insight into the meaning of our experimental results is obtained by explicitly computing the contributions of mass disorder and microscopic strain to the compositional dependence of the Raman modes. Starting with a pure material, for example Si, we can view the alloy formation as a two-step process. During the first step, the atomic masses are changed to reproduce the mass distribution in the real alloy, but no bond distortions are allowed. Since the phonon-dispersion curves of group-IV semiconductors scale very well with the ionic plasma frequency $\omega_{\text{pl}}\propto M^{-1/2}a^{-3/2}$, the force-constant changes in this step can be neglected. Hence the frequency shifts can be easily computed by considering large supercells with the same force-constant matrix as in the bulk, but with the alloy mass distribution. In the second step, the system is allowed to relax to its final equilibrium position. The microscopic strain dependence is then the difference between the experimental dependence and the mass disorder effect. This approach has been used in Refs. 21 and 31. Reference 21 uses a rigid ion model which provides a good fit of the phonon dispersion relations in bulk Si. Reference 31, on the other hand, utilizes a generalized Keating model. The mass disorder terms calculated from these models are quite different, suggesting that this term is very sensitive to the details of the phonon-dispersion curves. We have repeated these calculations using bulk Si force constants obtained from *ab initio* density-functional perturbation theory.[46] Phonons calculated with this method are in excellent agreement with experimental data for tetrahedral semiconductors. The mass disorder contributions obtained from the *ab initio* approach are shown in Table II. As in Ref. 21, the mass disorder term is found to be approximately linear in the alloy concentration. However, the numerical values of the slopes turn out to be very different from those calculated in Ref. 21, and much closer to those computed in Ref. 31. An interesting result from our theoretical simulations is that the C- and Ge-related mass disorder effects are additive for the Si-Si mode in $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ films. This provides strong support for our assumption of additivity of the C and Ge dependences of the modes, since the microscopic strain component is expected to be a linear function of the bond deformations.

It has been proposed[47] that the microscopic strain term can be represented by

$$\frac{\Delta\omega}{\omega}=-3\gamma\frac{\Delta R}{R}, \tag{7}$$

where γ is the Grüneisen parameter for the Raman mode, and ΔR is the change in nearest-neighbor bond lengths. In bulk materials under hydrostatic strain $\Delta R/R=\Delta a/a$, where Δa is the change in lattice constant, so that Eq. (7) reduces to the usual definition of the Grüneisen parameter γ, which for the zone-center optical phonon in tetrahedral semiconductors is very close to unity.[48] For alloy semiconductors, the relative changes in nearest-neighbor bond lengths are not necessarily equal to the relative changes in the lattice constant. Equation (7), which recognizes the fact that the frequency of optical phonons is dominated by nearest-neighbor bond stretching force constants, has been shown to correctly predict local mode frequencies in III-V semiconductor alloys.[47] These results suggest that Raman scattering can be used to establish the relationship between bond lengths and average lattice constants. This relationship can be formally written as[26,29]

$$\frac{\Delta R}{R}=(1-a^{**})\frac{\Delta a}{a}, \tag{8}$$

where a^{**} is the so-called topological rigidity parameter. In principle, a^{**} is a function of the bond type and composition. In the Pauling limit, where bond lengths are conserved, $a^{**}=1$. The opposite case $a^{**}=0$ is frequently referred to as Vegard's limit. The actual value of a^{**} in $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloys is controversial. Theory, in particular *ab initio* calculations,[15,26–28] predict values of the order of $a^{**}=0.4$–0.7 for the Ge-Ge as well as the Si-Si bonds. Early EXAFS measurements by Minomura *et al.*[22] yield $a^{**}=0.5$ for the Ge-Ge bond, in good agreement with theory. On the other hand, later results by Kajiyama *et al.* yield $a^{**}=1$.[24] EXAFS experiments on strained $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ layers by Woicik *et al.*[23] indicate that the epitaxial strain does not affect nearest-neighbor bond lengths, a result which appears to be consistent with the findings of Kajiyama *et al.*[24] However, more recent EXAFS experiments by Aldrich, Nemanich, and Saye, again indicate $a^{**}=0.6$ for the Ge-Ge bonds in $\mathrm{Si}_{1-x}\mathrm{Ge}_x$, in good agreement with theory.[25] The inconsistencies of the EXAFS results call for an independent test of bond-length predictions for group-IV alloys. Using Eqs. (7) and (8), the parameter a^{**} can be obtained from the microscopic strain terms in Table II. In order to estimate $\Delta a/a$ we take advantage of the fact that the lattice constant of $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloys follows Vegard's law quite closely. Using $\gamma=1$, we obtain $a^{**}=0.61$ for the Si-Si bond and $a^{**}=0.66$ for the Ge-Ge bond in these alloys, in very good agreement with the theoretical predictions. In the case of $\mathrm{Si}_{1-y}\mathrm{C}_y$ alloys, significant deviations from Vegard's law have been predicted.[13,15] While the Ge/C strain compensation for ratio is roughly 8/1 according to Vegard's law, Windl and Sankey[5] find that for small carbon concentrations the lattice constant is given by $a_{\text{Si-C}}=5.431-3.37y$ (in Å), which implies a compensation ratio of 15/1. Similarly, Kelires[13] predicts a compensation ratio of 11/1. Using the theoretically predicted lattice constants and $\gamma=1$, for the Si-Si bond in $\mathrm{Si}_{1-y}\mathrm{C}_y$ we obtain $a^{**}=0.62$ from Ref. 15 and $a^{**}=0.4$ from Ref. 13. The similar values of the topological rigidity parameter for the Si-Si bond in $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ and $\mathrm{Si}_{1-y}\mathrm{C}_y$ alloys, particularly when we use the lattice constant prediction from Windl and Sankey, suggest that in the ternary alloy $\mathrm{Si}_{1-x-y}\mathrm{Ge}_x\mathrm{C}_y$ (with 100% substitutional carbon) the microscopic strain term for the Si-Si mode may indeed vanish when C and Ge compensate for each other, so that the lattice constant of the ternary equals that of Si. This contradicts the conclusions of Ref. 21. The reasons for the discrepancy are now apparent: in Ref. 21, the mass disorder terms (and consequently, the microscopic strain terms) were computed from an empirical lattice dynamical model with insufficient accuracy. In addition, it was assumed that Vegard's law can be used to predict the lattice constant of $\mathrm{Si}_{1-y}\mathrm{C}_y$ alloys. The combined effect of these assumptions led to the conclusion that the Si-Si bond length may still be stretched when C is added to compensate for the epitaxial strain due to the Ge content. In contrast, our results here are consistent with the assumption that the Si-Si bonds relax to their equilibrium value in pure Si if the lattice constant of $\mathrm{Si}_{1-x-y}\mathrm{Ge}_x\mathrm{C}_y$ equals that of Si.

V. CONCLUSIONS

In this paper we have reported the carbon dependence of the Si-Si, Si-Ge, and Ge-Ge Raman mode frequencies in $\mathrm{Si}_{1-x-y}\mathrm{Ge}_x\mathrm{C}_y$ alloys. We find that these frequencies have a very strong carbon dependence, which can be explained in terms of the large compressive microscopic strain induced by the incorporation of carbon. In all samples, only a fraction of the carbon atoms has been confirmed to occupy substitutional sites, a finding that makes it difficult to compare the experimental Raman data with theoretical predictions for samples with 100% substitutional carbon. However, we find an intriguing agreement with theory when we plot our measured frequencies as a function of the substitutional carbon concentration y_{sub}. Moreover, this way of representing our experimental results leads to a unified description of the microscopic strain dependence of the modes as a function of both the Ge and C fractions. Our analysis suggests that Raman mode frequencies in semiconductor alloys are a sensitive probe of bond lengths in these systems.

ACKNOWLEDGMENTS

This work was supported by AFOSR (DARPA) under Grant No. F49620-93-C0081 and by the NSF under Grant Nos. DMR-9412550 and DMR-9521507. M.M.L. thanks the Organization of American States for financial support.

[*] On leave from Departamento de Física, CINVESTAV-IPN, Apdo. Postal 14-740 México D.F. 07000.

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