Structure and lattice dynamics of $Ge_{1-y}C_y$ alloys using anharmonic Keating modeling

C. Guedj* and J. Kolodzey

Department of Electrical and Computer Engineering, University of Delaware, Newark, Delaware 19716

A. Hairie

*Laboratoire d'Etudes et de Recherches sur les Matériaux, Institut des Sciences de la Matière et du Rayonnement,
UPRESA-CNRS 6004, 6 Boulevard du Maréchal Juin, 14050 Caen Cedex, France*

The incorporation of substitutional C into Ge is studied theoretically with an anharmonic Keating model fitted to recent experimental data and specifically adapted to the computation of the structural properties and the lattice dynamics of $Ge_{1-y}C_y$ alloys. In the range of physically realistic concentrations ($y < 3\%$), the change of lattice parameter due to substitutional carbon is found to agree with Vegard's law of linear interpolation between germanium and diamond with a maximum relative deviation less than 0.03%. This result is obtained in the case of a $Ge_{1-y}C_y$ alloy either random, diluted, or with C mostly arranged in third nearest neighbors. In the case of a pseudomorphic alloy on germanium (001), the tetragonal distortion of the lattice is well described (error $< 0.13\%$) if the elastic constants of the alloy are linearly interpolated between the corresponding parameters of bulk Ge and C in the framework of macroscopic linear elastic theory. The position of the localized vibrational mode of substitutional C in Ge depends on the distribution of carbon, and new phonon modes appear for certain atomic arrangements. Carbon atoms in first nearest neighbor positions give new modes around 425, 480, and 610 cm^{-1}, while a new GeC-like mode occurs at 487 cm^{-1}. C in third nearest neighbor (most stable) arrangements induce an additional mode around 550 cm^{-1}. A signature of the fifth nearest neighbor configuration is calculated around 510 cm^{-1}. This study suggests that the content of substitutional carbon in $Ge_{1-y}C_y$ alloys can be estimated from the lattice constant by x-ray diffraction for $y < 3\%$, and that the local order around C can be probed by Raman and infrared absorption spectroscopy. [S0163-1829(99)04046-1]

I. INTRODUCTION

Substitutional carbon incorporation into Si-Ge alloys seems to be promising for expanding the versatility of IV-IV semiconductor compounds and devices.[1] The Ge-Si-C alloy system is attractive for band gap and strain engineering of heterostructures.[2] Meanwhile, the lattice mismatch between C and Ge is very high (about 59%), the difference of electronegativity is important, and the solubility of C in Ge is very low (10^8 atoms/cm³ at the melting point of Ge).[3] Therefore, careful optimization of the growth parameters is required to obtain a material suitable for device applications. Several attempts to grow $Ge_{1-y}C_y$ alloys have been reported,[1,4–7] but it is clear that carbon is not always fully substitutional in Ge. A theoretical analysis may help to predict the properties of the perfectly substitutional alloy, and several papers have addressed this issue.[8,9] The prior theoretical work, however, lacked the availability of recent experimental data.[5] In this present contribution, our theoretical approach will be explained; then the results about the structural effects of substitutional C in Ge and the corresponding localized phonon spectra will be successively detailed.

II. THEORETICAL APPROACH

Theoretical modeling of $Si_{1-x-y}Ge_xC_y$ alloys must take into account the strong local distortion around C. Kelires used a Tersoff potential[10] and Monte Carlo simulations[11] to predict significant deviation of the structural parameters from linearly interpolated values. In Kelires' approach, the interatomic potential was fitted to the calculated[12] enthalpy of formation ($\Delta H \approx 0.2$ eV/atom) of the hypothetical zinc-blende Ge-C alloy. The precision of this value might be questionable, and this approach does not yield the precise lattice parameter of carbon-free compounds. Alternatively, Rücker and Methfessel[13] fitted their anharmonic Keating potential to the lattice parameters, elastic constants, and zone-center optical phonon frequencies of the elementary compounds. This variant of the well-known Keating model[14] is adapted to the description of elastic properties, phonon frequencies, and relaxed geometry when large distortions are involved. In comparison, a full *ab initio* calculation would require greater computational effort. In our approach, we have kept the formalism and scaling laws of Rücker and Methfessel, but we have precisely fitted the force constants to the lattice parameters ($a_{Ge} = 0.56576$ nm, $a_C = 0.356683$ nm) (Ref. 15) and phonon modes of Ge[16] and diamond[17] [$\Gamma_{LTO}(\Gamma_{25'})_{Ge} = 9.02$ THz, $\Gamma_{LTO}(\Gamma_{25'})_C = 39.9$ THz]. The anharmonic Keating coefficients used are listed in Table I. The very high precision and reliability of these experimental data, which can be obtained by x-ray diffraction, Raman spectrometry, and absorption spectroscopy, justify our approach. The calculated lattice parameters and phonon modes are intended to have a precision of 10^{-5} nm and 0.1 cm^{-1}, respectively. Our potential has been also tuned to fit the recently measured[5,6] localized vibrational mode of C in Ge (531 cm^{-1}) and the predicted lattice parameter (a_{GeC}) of the hypothetical zinc-blende GeC compound. We previously obtained[18] a value of a_{GeC}

TABLE I. Anharmonic Keating parameters α and β used for the calculations. Force constants and lattice constants are given in atomic units. The values in parentheses [Rücker and Methfessel, Phys. Rev. B **53**, 3 (1996)] are given for comparison.

	a_0	α	β
C	6.7424 (6.68)	0.143 (0.137)	0.101 (0.101)
Ge	10.695 (10.66)	0.0555 (0.049)	0.015 (0.015)
GeC	8.54 (8.54)	0.0742 (0.081)	0.031 (0.031)

$\approx 0.451\,76$ nm using a method similar to Ref. 19. The corresponding values found in the literature[19,9] are also close to 0.45 nm. To simulate the structure, molecular dynamics relaxation is calculated from a 512 atom cubic supercell by time increments of 3 fs, until the total potential energy reaches a stable minimum. To model the fully relaxed (i.e., virtually substrate-free) alloy, we have computed isotropic relaxations, where no external pressure is applied to the computational box. In addition, we have investigated pseudomorphic Ge$_{1-y}$C$_y$ alloys on Ge(001) to compare with recent experiments. By definition, the parallel lattice parameter of the supercell is maintained to the value of Ge here. In a further stage, the local phonon density around carbon is computed, using the recursion method detailed in Ref. 20. With standards notations, if the Green function for a given atom i and direction x is given by

$$G(\omega^2) = \left\langle i,x \left| \frac{1}{D - I\omega^2} \right| i,x \right\rangle, \qquad (1)$$

then the local phonon density of state is defined by[20]

$$Y(\omega^2) = -\frac{1}{\pi} \lim_{\delta \to 0} \text{Im}[G(\omega^2 + i\delta)]. \qquad (2)$$

The recursion method permits to compute in a few steps a continuous fraction which approximates the Green function, thus enabling a convenient computation of the local phonon density of state for each atom. The calculated spectra can be compared with absorption spectroscopy and Raman spectrometry data after application of the proper selection rules. Several carbon distributions have been tested: random, diluted, and 3nn. By definition, the diluted distribution is obtained when the minimum distance between two carbon atoms is above 1 nm. The 3nn distribution corresponds to carbon atoms mostly in third nearest neighbor arrangements. This latter configuration is the most stable, in agreement with Refs. 13 and 9. The results presented here are typically averaged on 12 analogous distributions.

III. RESULTS AND DISCUSSION

A. Microstructure

The extension of the local distortion around an individual C in the cubic supercell of 512 atoms is depicted in Fig. 1. The average distance between C and its first Ge neighbors is 0.213 62 nm, which is about 13% smaller than the Ge-Ge distance in pure Ge. The distortion is visible at the second nearest neighbor, but is attenuated after the third. Between the second and the third nearest neighbor, the Ge-Ge bond
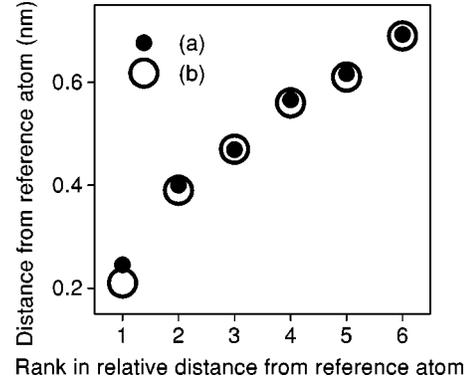

FIG. 1. Relative distance between nearest neigbors computed for (a) pure Ge, (b) one substitutional carbon atom surrounded by Ge in a cubic supercell of 512 atoms.

length increases to elastically accommodate the carbon-induced perturbation. It is clear that the carbon distortion is localized, and there is a local departure from a perfect translational symmetry, which induces a localized vibrational phonon mode studied below. This localized strain modifies the size of the supercell, and the average size along [001] gives the perpendicular lattice parameters represented in Fig. 2. In the case of isotropically relaxed alloys [Figs. 2(a) to 2(d)], the evolution of perpendicular (and parallel) lattice parameters follows Vegard's law (within 0.03%) up to 3% C, whatever the atomic distribution of C. This might appear surprising, since the lattice parameter of the reference zinc-blende GeC compound ($a_{\text{GeC}} \approx 0.451\,76$ nm) is smaller than the linear interpolation between Ge and C ($\approx 0.461\,22$ nm). Actually, for the Ge$_{0.5}$C$_{0.5}$ alloy, we found that the statistical distribution of C has a strong influence on the lattice parameter. By comparison, the departure from Vegard's law is maximum around 50% Ge in Si-Ge alloy. The probability to form the SiGe ordered structure (with a smaller lattice parameter) may explain the measured deviation. For GeC alloys, Vegard's law does not apply to the
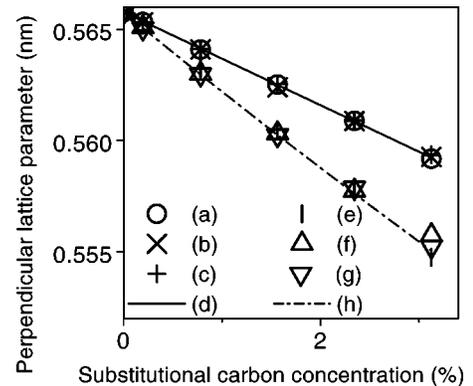

FIG. 2. Evolution of the perpendicular lattice parameter after incorporation of substitutional C in Ge. Several statistical distributions of C are considered: (a) C replacing Ge in a random alloy; (b) a diluted alloy, defined as when the interatomic distance between two carbon atoms is superior to 1 nm; (c) for carbon atoms mostly in third nearest neighbors (3 nn), the most stable (lowest energy) configuration; (d) the linear interpolation of the lattice parameters of Ge and diamond (Vegard's law). Curves (e)–(h) are analogous, except that the layer is pseudomorphic on Ge(001).

zinc-blende (1:1) compound, but this interpolation is reasonably accurate around Ge and diamond. Therefore it is possible to estimate accurately the substitutional carbon content of $Ge_{1-y}C_y$ alloys of low carbon content ($<3\%$) by measuring the lattice parameter with x-ray diffraction.[21,22] In the general case, the deviation from Vegard's law may depend on atomic distributions, especially around the regions of possible ordered compounds. This trend is exacerbated in the case of pseudomorphic layers on Ge (001). From Figs. 2(e) to 2(h), it is clear that the perpendicular lattice parameters (hence the elastic constants of the alloy) depend on the atomic distribution of atoms; therefore the atomic distribution of C modifies the relaxation process in the pseudomorphic lattice. Experimentally, the atomic distribution of atoms may depend on the growth process; therefore the elastic constants might also depend on the sample preparation. In all cases, a linear interpolation between the elastic constants and lattice parameters within the frame of macroscopic linear elastic theory [Fig. 2(h)] gives the perpendicular lattice parameter within a reasonable error ($<0.13\%$). This means that the relationship between the relaxed, parallel, and perpendicular lattice parameters (a_0, $a_\parallel$, $a_\perp$) may be expressed as

$$a_0 = a_\perp \left(\frac{1 + K a_\parallel / a_\perp}{1 + K} \right), \tag{3}$$

where

$$K = 2 \frac{\nu}{1-\nu} = 2 \frac{C_{12}}{C_{11}} \tag{4}$$

is the elastic correction factor and ν the Poisson ratio of the $Ge_{1-y}C_y$ alloy (with $y < 3\%$). The departure from this law is maximum for the diluted alloy, where carbon atoms have nearly no interaction with each other. We conclude that the proximity of carbon atoms affects the global distortion of the pseudomorphic lattice. The cooperative effect of two close carbons seems to be superior to the sum of the effects of two isolated ones. The most probable (3nn) configuration gives a lattice parameter close to linear interpolation. The extrapolation to higher carbon concentrations increases the statistical spreading in lattice parameters and the subsequent deviations from Vegard's law, especially around the concentrations of possible ordered compounds.

B. Phonon spectra

The computation of phonon spectra is a further basic tool to investigate this new material. In Fig. 3, the localized vibrational spectra around C are computed in the case of an isotropically relaxed supercell containing two substitutional carbon atoms, for increasing C-C distance. In a way similar to $Si_{1-x}C_x$ alloys, novel modes appear for certain configurations. Localized vibrational spectra are sensitive to the local order and provide a powerful probe[8] of the bonding configuration. The 1nn configuration (improbable) gives new modes at 425, 480, and 610 cm^{-1}. GeC-like modes (2nn) are characterized by signatures at 487 and 540 cm^{-1}. The 3nn additional mode is around 550 cm^{-1}. Another additional feature, provided from the 5nn configuration, is situated around 510 cm^{-1}. Physically, these spectra can be considered as a
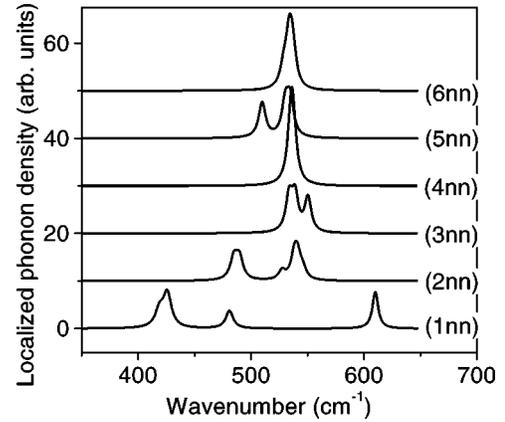

FIG. 3. Localized phonon density spectra around C calculated by the recursion method in the case of an isotropically relaxed supercell containing two carbon atoms. Curves (1nn)–(6nn) are calculated for increasing distance between C. With standard notation, "1nn" means that the two carbon atoms are arranged in first nearest neighbors. The width of the peaks can be numerically tuned; it is given for comparison purposes only.

result of complex conjugated elastic interactions involving close neighbors. The wave numbers depend slightly on the C content and the lattice strain. The shift of the main localized vibrational mode (LVM) of substitutional C in Ge (around 530 cm^{-1}) depends upon the atomic distribution (Fig. 4). The local order may depend on the growth parameters, and there is no *a priori* shift of the mode with substitutional C content. In all cases, for low carbon contents, the LVM wave number of the pseudomorphic layer (around 529 cm^{-1}) is lower than its relaxed counterpart (around 531 cm^{-1}),[5,6] which is observed experimentally.

IV. SUMMARY

In summary, we have performed molecular dynamics simulations using a valence force field model to simulate the incorporation of C into substitutional sites of Ge. In the case of relaxed alloys, the lattice parameter follows Vegard's law
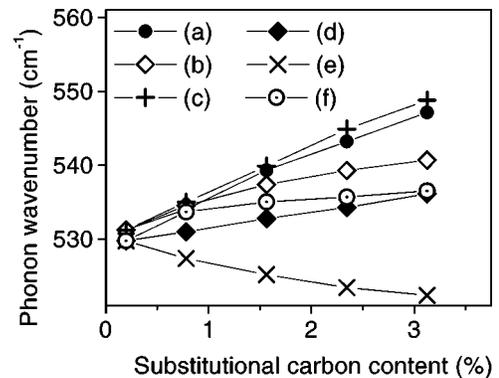

FIG. 4. Frequencies of localized phonon spectra around C calculated by the recursion method for increasing C content and various statistical distributions of substitutional C. Curves (a)–(c) are calculated for a random, diluted, and 3nn configuration, respectively, in the case of an isotropically relaxed alloy. The homologous curves (d)–(f) are computed for a pseudomorphic layer on Ge(001). The lines are displayed to guide the eyes only.

with a good accuracy (less than 0.03% error) up to at least 3% C, whatever the substitutional carbon distribution. Hence the carbon content can be successfully estimated through the measurement of lattice parameters by x-ray diffraction. The linear interpolation of elastic constants and lattice parameters of Ge and diamond gives a valuable estimate (error $<0.13\%$) of the perpendicular lattice parameter of the alloy within the framework of macroscopic linear elastic theory. The influence of the distribution statistics increases with C concentration, and a departure from Vegard's law is obtained around the region of possible ordered compounds (like zinc-blende GeC). The relative position of carbon neighbors influences the localized phonon spectrum, and the shift of the LVM wave number with C strongly depends on the carbon distribution. This study provides reference analytical formulas applying to the perfect Ge$_{1-y}$C$_y$ substitutional alloy. The predicted phonon spectra are a fundamental basis to probe the local order in this new material, which might play an important role in future IV-IV microelectronics and opto-electronics.

*Author to whom correspondence should be addressed: CyrilGuedj@hotmail.com

[1] K. Brunner, K. Eberl, W. Winter, and E. Bugiel, Appl. Surf. Sci. **102**, 17 (1996).

[2] K. Eberl, S.S. Iyer, S. Zollner, J.C. Tsang, and F.K. Le Goues, Appl. Phys. Lett. **60**, 3033 (1992).

[3] R.I. Scace and G. Slack, J. Chem. Phys. **30**, 1551 (1959).

[4] H.J. Osten, E. Bugiel, and P. Zaumseil, J. Cryst. Growth **142**, 322 (1994).

[5] L. Hoffmann, J.C. Bach, B. Bech Nielsen, P. Leary, R. Jones, and S. Öberg, Phys. Rev. B **55**, 11 714 (1997).

[6] W.H. Weber, B.K. Yang, and M. Krishnamurthy, Appl. Phys. Lett. **73**, 626 (1998).

[7] J. Kolodzey, P.A. O'Neil, S. Zhang, B.A. Orner, K. Roe, K.M. Unruh, C.P. Swann, M.M. Waite, and S. Ismat Shah, Appl. Phys. Lett. **67**, 13 (1995).

[8] H. Rücker, M. Methfessel, B. Dietrich, K. Pressel, and H.J. Osten, Phys. Rev. B **53**, 1302 (1996).

[9] P.C. Kelires, Appl. Surf. Sci. **102**, 12 (1996).

[10] J. Tersoff, Phys. Rev. B **39**, 5566 (1989).

[11] P.C. Kelires, Phys. Rev. Lett. **75**, 1114 (1995).

[12] P.C. Kelires and P.J.H. Denteneer (unpublished).

[13] H. Rücker and M. Methfessel, Phys. Rev. B **52**, 11 059 (1995).

[14] P.N. Keating, Phys. Rev. **145**, 637 (1966).

[15] W. Kaiser and W.L. Bond, Phys. Rev. **115**, 857 (1959).

[16] G. Nilsson and G. Nelin, Phys. Rev. B **6**, 3777 (1972).

[17] S.A. Solin and A.K. Ramdas, Phys. Rev. B **1**, 1687 (1970).

[18] C. Guedj (unpublished).

[19] O.F. Sankey, A.A. Demkov, W.T. Petuskey, and P.F. McMillan, Modell. Simul. Mater. Sci. Eng. **1**, 741 (1993).

[20] A. Hairie, F. Hairie, G. Nouet, E. Paumier, and A.P. Sutton, in *Polycrystalline Semiconductors III—Physics and Technology*, edited by H.P. Strunk, J.H. Werner, B. Fortin, and O. Bonnaud (Trans Tech, Aedermannsdorf, Switzerland, 1993), Vol. 37-38, p. 91.

[21] J.P. Dismukes, L. Ekstrom, and R.J. Paff, J. Phys. Chem. **68**, 3021 (1964).

[22] R. Duschl, O.G. Schmidt, W. Winter, K. Eberl, M.W. Dashiell, J. Kolodzey, N.Y. Jin-Phillipp, and F. Phillipp, Appl. Phys. Lett. **74**, 1150 (1999).