

Substitutional Ge in 3C–SiC

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The incorporation of substitutional Ge into 3C–SiC alloys is studied theoretically with an anharmonic Keating model specifically adapted to the computation of the structural properties and the lattice dynamics of $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ alloys. Basic energy calculations show that the substitution of Si by Ge is more probable than the substitution of C by Ge in the zinc-blende silicon carbide crystal. If Ge replaces only Si, then the lattice parameter equals $(0.43593 \pm 0.00002) + (0.000337 \pm 0.000002)y$, where y stands for the Ge content. Hence, Vegard's law is not applicable. The alloy is characterized by a distinct phonon spectrum whose maximum peak position in cm^{-1} is best described by the exponential decay $(243 \pm 1) + (27 \pm 2)\exp[-y/(7.5 \pm 1.2)]$ up to the zinc-blende GeC compound. © 1999 American Institute of Physics. [S0003-6951(99)01305-4]

Silicon carbide (SiC)-based electronics are suitable for high-power and high-frequency applications, as well as for severe environments, including high temperature and high radiation.^{1,2} Silicon carbide's ability to function under such extreme conditions is expected to enable significant improvements in a far ranging variety of applications and systems. Substitutional Ge may modify the structural, electrical, and optical properties of SiC-based heterostructures, therefore, Ge incorporation into SiC-based microelectronics and optoelectronics may provide³ further device opportunities through band-gap and strain engineering. The crystal growth might not be simple, mainly because of the difference in lattice parameters and covalent radii between silicon germanium and diamond, but Ge seems to have a beneficial effect on the epitaxy of single-crystalline 3C–SiC on silicon.⁴ There are few if any data available about substitutional Ge in 3C–SiC to our knowledge.⁴ Because of the broad technological importance of IV–IV materials and devices, as well as the increasing ability to grow highly metastable alloys, it is essential to develop theoretical predictions of the physical properties of this material.

The understanding of the lattice-vibrational properties is important to explain various interesting properties of SiC, among them mechanical, thermal, and structural ones. For example, phonons may stabilize the polytypism via several contributions to the free energy.⁵ Here, the structural properties and lattice dynamics of substitutional Ge in 3C–SiC are determined using a modified anharmonic Keating model specially adapted to the computation of lattice parameters and phonon spectra of $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ alloys. First, the theoretical model will be briefly described, then the structural effects of substitutional Ge in 3C–SiC and the corresponding localized vibrational spectra will be successively detailed.

Our theoretical approach is based upon a valence force-field model derived from Keating⁶ and taking into account the effects of carbon anharmonicity. The interactions between atoms have been modeled with an interatomic potential similar to the one of Rucker *et al.*⁷ with the exception of

adjusting our force coefficients to yield the correct lattice parameters and phonon modes of Si, Ge, $\text{Si}_{1-x}\text{Ge}_x$, diamond, and 3C–SiC at 300 K. Our model gives a localized vibrational mode of C in pure Ge situated at 531 cm^{-1} , in agreement with Hoffmann *et al.*⁸ The very high precision and reliability of these experimental data, which can be obtained by x-ray diffractometry, Raman spectrometry, and absorption spectroscopy, justify our approach. In addition, our set of parameters enables the computation of the LO(T) mode from 3C–SiC, which cannot be obtained from the parameters given by Rucker *et al.*,⁷ to our knowledge. This model is, therefore, ideally suited to a precise computation of lattice parameters and phonon spectra of tetrahedrally coordinated $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ alloys. The molecular dynamics relaxation is calculated from a 512 atom supercell by time increments of 3 fs, until the total potential energy reaches a stable minimum. We have computed isotropic relaxations, where no external pressure is applied to the computational box, to simulate the structural properties of the alloy. In a further stage, the local phonon density around carbon is computed, using the recursion method detailed in Ref. 9. This algorithm enables the computation of the local phonon density around chosen atoms. The calculated spectra can be compared with absorption spectroscopy and Raman spectrometry results after application of proper selection rules. Numerous atomic configurations have been tested, in order to simulate the substitution of Ge into the 3C–SiC crystal.

The application of these theoretical tools gives an insight into the structure of the substitutional alloy. In the case of a single substitutional Ge into the zinc-blende SiC matrix, the atomic positions after isotropic relaxation are depicted in Fig. 1. The substitution of C by Ge induces a higher lattice distortion than the substitution of Si, which is logical because Ge is close to Si in terms of atomic radius, electronegativity, and elastic properties. The substitution of C requires at least 38 times more energy, therefore, it is highly unprobable. Silicon carbide is more rigid than silicon, therefore, the distortions are confined across few atomic distances. This strain modifies the crystal dimensions, in a manner depending on the statistical atomic distribution. The lattice param-

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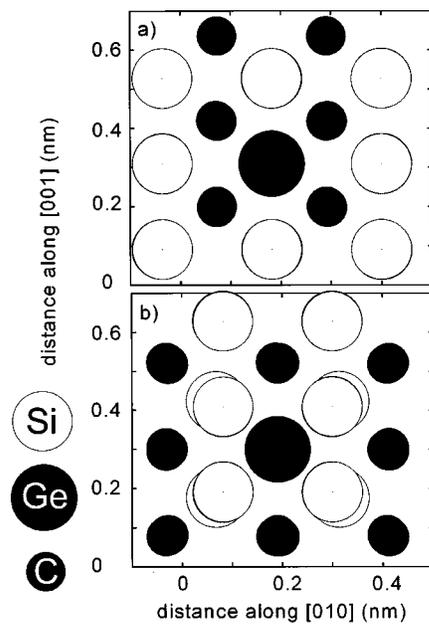


FIG. 1. View along [100] of a substitutional Ge into 3C-SiC. Molecular dynamics computation is used to relax the 512 atoms supercell isotropically. C, Si, and Ge are represented with spots of increasing diameter. (a) is obtained when Ge replaces Si, while (b) corresponds to the substitution of C by Ge. A modified Keating model which takes into account the anharmonicity of C is used to compute the atomic interactions.

eter is obviously proportional to the mean size of the supercell after relaxation, and the results are displayed in Fig. 2. If we assume that Ge replaces Si only [Fig. 2(a)], then the lattice parameter equals $(0.43593 \pm 0.00002) + (0.000337 \pm 0.000002)y$, where y stands for the Ge content. A Vegard's law [Fig. 2(b)] between Ge and cubic SiC would give a lattice parameter of $0.43596 + 0.0012994x$. Even in the hypothesis of a random substitution of Si or C by Ge [Fig. 2(c)], Vegard's law does not apply. In the case of a random substitution, the increase of the lattice parameter is rapid, but the corresponding increase of elastic energy is unlikely to be observed experimentally, because more stable atomic arrangements will occur instead. In any case, the modification of the lattice parameter induced by substitutional Ge in 3C-SiC should be easily probed by x-ray diffraction.

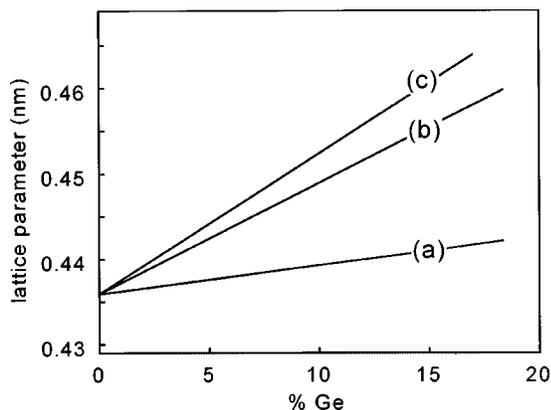


FIG. 2. Evolution of the lattice parameter after incorporation of substitutional Ge in 3C-SiC. (a) is obtained when Ge replaces only Si in a random manner. (b) is computed using a linear combination of the lattice parameters of Si, Ge, and diamond, considering the relative concentrations (Vegard's law). (c) is obtained when Ge replaces Si or C randomly.

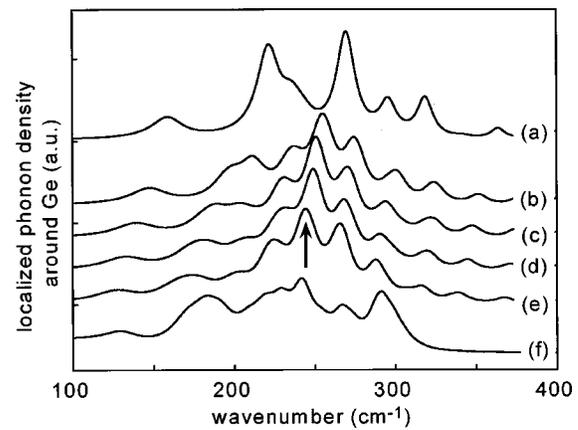


FIG. 3. Localized phonon spectra around Ge calculated by the recursion method. Ge is assumed to replace only Si in the zinc-blende 3C-SiC crystal. Curves (a)-(f) are calculated for increasing substitutional Ge concentrations (respectively, 0.2%, 4.9%, 9.4%, 14.8%, 18.4%, and 50%).

The computation of phonon spectra give a further tool to investigate this material. In Figs. 3(a)-3(f), the localized vibrational spectra around Ge are computed for increasing Ge content. The substitutional incorporation of Ge in 3C-SiC is characterized by a distinct phonon spectrum whose maximum peak position in cm^{-1} is best described by the exponential decay $(243 \pm 1) + (27 \pm 2)\exp[-y/(7.5 \pm 1.2)]$ up to the zinc-blende GeC compound. Because of the strong local elastic heterogeneity, the calculated spectrum is usually complex, and the clear maximum obtained in curve (e) of Fig. 3 is marked by an arrow. In the real crystal, a smoothing of the spectrum should naturally occur because of the very high number of atoms involved. Hence, our fit assumes an additional Gaussian smoothing. Physically, these spectra could be considered as a result of complex multiphonon processes involving the nearest neighbors of Ge. The Ge-C bond is stabilized in the zinc-blende GeC compound, therefore, it is reasonable that the fitted phonon energy decreases when the Ge concentration increases. According to the lattice dynamics calculations, this peak should be Raman active. Hence, proper substitutional Ge incorporation into 3C-SiC could be assessed by Raman spectrometry.

In summary, we have performed molecular dynamics simulations using a valence force-field model to simulate the incorporation of Ge into substitutional sites of 3C-SiC. The silicon site is energetically favored over its C counterpart for the Ge substitution, and the lattice parameter is expected to deviate from Vegard's law. If Ge replaces only Si, then the calculated lattice parameter equals $(0.43593 \pm 0.00002) + (0.000337 \pm 0.000002)y$, where y stands for the Ge content. The alloy is characterized by a distinct phonon spectrum whose maximum peak position in cm^{-1} is best described by the exponential decay $(243 \pm 1) + (27 \pm 2) \times \exp[-y/(7.5 \pm 1.2)]$ up to the zinc-blende GeC compound. This mode should be Raman active. Ge-doped silicon carbide, which can be probed by x-ray diffraction and Raman spectrometry, might play an important role in future IV-IV microelectronics and optoelectronics.

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