

COMMUNICATIONS

Precipitation of β -SiC in $\text{Si}_{1-y}\text{C}_y$ alloys

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(Received 26 March 1998; accepted for publication 7 July 1998)

The infrared modes of annealed $\text{Si}_{1-y}\text{C}_y$ alloys were studied experimentally and theoretically. The alloys were grown on Si(100) substrates by solid-source molecular beam epitaxy and were characterized by Fourier transform infrared spectroscopy. At annealing temperatures above 850 °C, the localized vibrational mode of substitutional C around 605 cm^{-1} diminished in intensity while another mode due to incoherent silicon carbide precipitates appeared at 810 cm^{-1} . For lower processing temperatures, a peak around 725 cm^{-1} has been tentatively attributed to a C-rich phase, which is a precursor to SiC precipitation. Theoretical calculations based on the anharmonic Keating model predict that small (1 nm) 3C-SiC *coherent* precipitates may actually produce a mode at 725 cm^{-1} . This mode occurs if the bonds gradually vary in length between the C-rich region and the host lattice. On the other hand, if the bonds are abruptly distorted at the edges of the precipitate, it becomes elastically isolated from the host lattice, and the 810 cm^{-1} mode appears. This study yields a picture of the thermal stability of dilute SiC alloys, which is important for the high-temperature processing steps necessary for device applications. Moreover, the coherent precipitation may provide a controllable way to form self-assembled 3C-SiC quantum dots into silicon germanium carbon alloys. © 1998 American Institute of Physics.[S0021-8979(98)08219-X]

Carbon incorporation into silicon-based microelectronics and optoelectronics provides device opportunities through band-gap and strain engineering,¹ and diffusion control. Substitutional carbon modifies the alloy band structure and the band offsets for Si-based heterostructures.^{2,3} In the dilute limit, the lowest-energy configuration for C atoms is the occupation of substitutional sites,⁴ where the carbon atoms are tetrahedrally bound to Si atoms. The difference in lattice parameters and covalent radii between silicon and diamond induce high bond distortions, which results in a modification of the phonon spectrum.⁵ In the limit of the highly diluted $\text{Si}_{1-y}\text{C}_y$ alloy, substitutional carbon gives a signature situated around 605 cm^{-1} . This localized vibrational mode can be observed either by absorption spectroscopy⁶ or by Raman spectroscopy.^{5,7,8} After thermal annealings at high temperatures (>900 °C), a broad peak around 810 cm^{-1} has been observed by several groups.^{6,9,10,11} This phenomenon is usually attributed to silicon carbide precipitation.¹¹ This result is naturally expected since the solubility of C in Si is $3 \times 10^{17} \text{ cm}^{-3}$ at the melting point¹¹ and stoichiometric SiC is the only thermodynamically stable structure in the Si-C system.¹² An additional vibrational mode situated around 725 cm^{-1} has been recently observed¹³ by infrared absorp-

tion spectroscopy for intermediate growth temperatures (~650 °C). This peak is consistent with a Si-C transitional phase, intermediate between the loss of substitutional C sites on the silicon lattice and the formation of SiC-relaxed precipitates. Here, we use a theoretical approach to demonstrate that the *coherent* precipitation of 3C-SiC in Si produces a vibrational mode situated between 700 and 740 cm^{-1} because of the strain-affected chemical bonds around C. The phonon mode around 810 cm^{-1} is obtained only in the case of *incoherent* precipitates. The latter case is characterized by the absence of crystalline continuity between the precipitates and the surrounding matrix, and the interface strain between 3C-SiC and Si may be accommodated by defects.

Our theoretical approach is based upon a valence force field model derived from Keating¹⁴ 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.*⁵ with the exception of adjusting our force coefficients to yield the correct lattice parameters and phonon modes of Si, diamond (in the Fd3m structure) and 3C-SiC at 300 K. This choice is justified by the very high precision and reliability of these experimental data, which can be obtained by x-ray diffraction, Raman spectroscopy, and absorption spectroscopy at room temperature. In addition, our set of parameters enables the computa-

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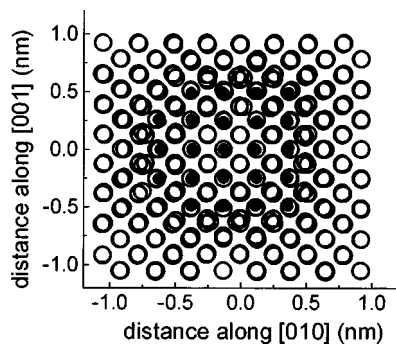


FIG. 1. View along $[100]$ of a 3C-SiC coherent precipitate coherently embedded into silicon and containing 50 carbon atoms. Molecular dynamics computation is used to relax the 512 atom supercell isotropically. The solid and open spots stand for C and Si, respectively. A modified Keating model, which takes into account the anharmonicity of C, is used to model the atomic interactions.

tion of the $LO(\Gamma)$ mode from 3C-SiC, which cannot be obtained from the parameters given by Rucker *et al.*⁵ to the best of our knowledge. Our model is, therefore, ideally suited to a precise computation of lattice parameters and phonon spectra of tetrahedrally coordinated $Si_{1-y}C_y$ 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 both isotropic relaxations, where no external pressure is applied to the computational box, and pseudomorphic relaxations, to simulate a fully strained layer on silicon. In a further stage, the local phonon density around carbon is computed, using the recursion method detailed in Ref. 15. This algorithm enables the computation of the local phonon density around chosen atoms. The calculated spectra can be compared with absorption spectroscopy and Raman spectroscopy results after application of proper selection rules. Numerous random and ordered atomic configurations have been tested, in order to simulate the precipitation of 3C-SiC into silicon.

The application of these theoretical tools gives the following results. In the case of a 3C-SiC precipitate containing 50 carbon atoms and coherently embedded into a silicon matrix, the atomic positions after isotropic relaxation are depicted in Fig. 1. The high bond distortions of this quantum dot are clearly evident, especially around the precipitate. From that picture, it is clear that the interface energy between the matrix and the precipitate is important, in agreement with Taylor *et al.*¹⁶ Silicon carbide is more rigid than silicon, therefore, the interface between the silicon and 3C-SiC is very abrupt, and the distortion occurs across few atomic distances. The statistical distribution of Si-C bonds is represented in Fig. 2. The distribution is broadened and asymmetrically distorted by the silicon-related strain. The Gaussian fit is centered around 0.208 nm, which is between 3C-SiC (0.188 nm) and Si (0.235 nm). The more distorted bonds can reach up to 0.235 nm at the interface between the matrix and the precipitate. This local departure from perfect crystalline periodicity gives an intense phonon mode, illustrated in Fig. 3(b). This spectrum is roughly composed of the classical localized vibrational mode around 605 cm^{-1} , a

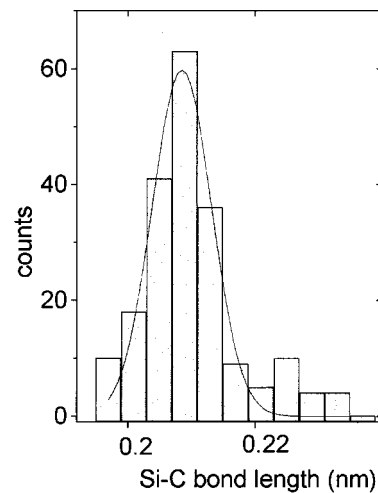


FIG. 2. Statistical distribution of Si-C bonds in the 3C-SiC precipitate of Fig. 1. A Gaussian fit of the distribution is centered around 0.208 nm. The calculated bond length can reach up to 0.235 nm. For comparison, the Si-C bond length in pure 3C-SiC is 0.188 nm.

small peak around 660 cm^{-1} , and a well-defined mode at about 725 cm^{-1} . Silicon-carbon bonds situated about one spherical monolayer inside the outermost frontier of the precipitate give the most intense phonon modes around 725 cm^{-1} . Curve (c) in Fig. 3 represents the local phonon density spectra averaged to all carbon atoms in the supercell. The 605 cm^{-1} localized vibrational mode is spread toward higher wavenumbers because of the high tensile strain, and the 725 cm^{-1} peak is present. These simulations are in reasonable agreement with the experimental absorption spectroscopy spectrum depicted in Fig. 3(a). The position of the mode depends upon the size of the 3C-SiC quantum dot and the strain around the precipitate. If the supercell is pseudomorphic to silicon, then the peak is situated around 560 cm^{-1} . The potential energy of the system is well fitted by a sigmoidal (Boltzman) increasing function of the precipitate size, and the phonon peak shifts toward higher energies

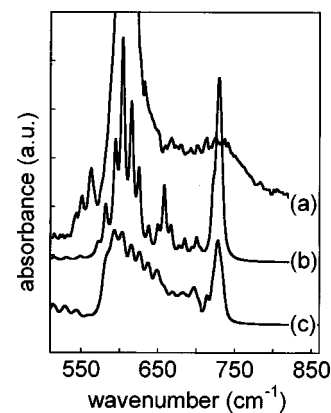


FIG. 3. Comparison between the experimental infrared absorption spectrum and the local phonon density calculated by the recursion method, for the 3C-SiC precipitate illustrated in Fig. 1. The experimental curve (a) is obtained with a $Si_{1-y}C_y$ sample grown by molecular beam epitaxy at $650\text{ }^\circ\text{C}$. The simulated curve (b) is calculated around a single carbon atom situated at the interface between the precipitate and its surrounding matrix, while (c) is the phonon spectrum averaged over all carbon atoms in the precipitate.

when the size increases or when the precipitate becomes incoherent to its matrix. The mode observed at 725 cm^{-1} is best matched in energy by the phonon spectrum of a spherical quantum dot containing about 50 carbon atoms and coherently embedded into an isotropically relaxed matrix.

Now, we propose the following interpretation for the physical behavior of substitutional carbon into silicon (or silicon germanium) alloys during thermal annealing. For rapid thermal annealings above $1000\text{ }^{\circ}\text{C}$ during a few seconds or at temperatures higher than $850\text{ }^{\circ}\text{C}$ for several hours, the formation of relaxed silicon carbide precipitates seems to be unanimously accepted.^{6,9–11} This process is attributed to thermally activated carbon diffusion, followed by precipitation. The interface between 3C–SiC and the matrix is defective, and the nanoprecipitates are relaxed. Our calculations show that if the precipitate were coherent, then the Si–C bond length would increase up to 25% at the interface. Temperature is linked to atomic agitation, therefore, structural defects are very likely to occur at the interface for high thermal atomic vibrations. Various types of defects may be involved, either with carbon, oxygen, or other complexes. For intermediate processing temperatures (between 600 and $850\text{ }^{\circ}\text{C}$ approximately), we suggest that substitutional carbon should have an increasing probability to jump into interstitial sites, for example, by forming a Si–C interstitial complex. It may, thereafter, produce a vacancy. Then, it could rapidly diffuse to form small-sized coherent precipitates, surrounded by a vacancy-rich matrix. The formation of such quantum dots may also depend on surface effects during the metastable growth. The additional presence of various defects might not be completely excluded, and thorough investigations have to be performed to further evaluate their nature and their density. The strain may be roughly maintained if the precipitates are coherent, because the crystalline periodicity is not completely disrupted. For obvious reasons, local elastic energy and Si–C bonds maximal distortions cannot increase indefinitely, therefore, such coherent precipitates should be highly metastable. A simulated size of $\sim 1\text{ nm}$ best matches our infrared absorption experimental results, therefore, the critical radius for loss of coherency of β -SiC in Si should be superior to 1 nm for our growth conditions. Similar results have been observed with silicon germanium carbon alloys. This mechanism of coherent precipitation may

provide a controllable way to form self-assembled quantum dots of $\sim 1\text{ nm}$ size, which can be observed by absorption spectroscopy.

In summary, we have performed molecular dynamics simulations using a valence force field model to simulate the silicon carbide precipitation into silicon. The recently measured¹³ phonon mode situated around 725 cm^{-1} is computed in the case of a *coherent* 3C–SiC precipitate isotropically relaxed. This picture is consistent with $\sim 1\text{ nm}$ β -SiC quantum dots coherently embedded into a vacancy-rich matrix. The phonon mode around 810 cm^{-1} is obtained only if the silicon carbide nanoprecipitates are *incoherent*. This mechanism of coherent precipitation may provide a controllable way to form self-assembled β -SiC quantum dots in silicon germanium carbon alloys.

The authors gratefully acknowledge support from ARO under Grant No. DAAH04-95-1-0625, and DARPA Contract No. F49620-96-C-0006.

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