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# Anharmonicity and local lattice distortion in strained Ge-dilute $Si_{1-x}Ge_x$ alloy

Juncai Dong, Zhiying Guo, Xiaoli Zhang, Pengfei An, Yu Gong, Hailiang Zhu, Pengshan Li, Dongliang Chen*

*Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China*

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ABSTRACT

We have investigated the anharmonicity and local lattice distortion in strained Ge-dilute $Si_{1-x}Ge_x$ alloy using Ge *K*-edge extended x-ray absorption fine structure measurement coupled with *ab initio* molecular dynamics simulation. Pronounced asymmetry is for the first time revealed for the Ge–Si first nearest-neighbor (NN) distribution even at room temperature, in good agreement with theoretical simulations. In comparison with harmonic approximation, the anharmonicity contributes an additional shift of 0.011 Å to the Ge–Si first NN bond distance, which is further found to be crucial to the qualitative change (i.e., contracting or stretching) of the Ge–Si second NN bond distance relative to the corresponding Si–Si bond distance in bulk Si. As the modifications of higher NN shells arise from the competition between the NN bond-distance stretching and the tetrahedral bond-angle deviation, those results indicate that the anharmonicity is critical in the proper determination of the local strain accommodation mode and thus the substrate effect. Farther NN shells exhibit slight asymmetry. Our findings reconcile the long-standing controversy regarding the dominant local strain relaxation mechanism in strained Ge-dilute $Si_{1-x}Ge_x$ alloys.

## 1. Introduction

In the last decades, considerable attentions have been paid to crystalline $Si_{1-x}Ge_x$ alloys and heterostructures due to their potential applications in band gap engineering and high-speed electronic devices with relatively simple incorporation into existing Si technology [1,2]. Because the electronic and optical properties of $Si_{1-x}Ge_x$ alloys can be tuned with composition $x$ between those of pure Si and pure Ge [3–5], from a structural point of view, it is of fundamental importance that how the significant strain arising from the 4.2% lattice mismatch and possible growth defects is accommodated in the atomic structure of this IV–IV binary alloy. In contrast to many III–V ternary alloys (e.g., $Ga_{1-x}In_xAs$ and $Ga_{1-x}In_xP$) whose lattice constants exhibit a linear dependence on composition $x$ in accordance with Vegard's law [6], the lattice constants of $Si_{1-x}Ge_x$ alloys are negatively deviated from an exact linear relation in the vicinity of $x = 0.5$ [7,8]. Microscopic properties such as the nearest-neighbor (NN) bond distances of Si–Si, Si–Ge, and Ge–Ge pairs show also different weak dependence on composition $x$ [7,9]. Those anomalous behaviors are beyond the conventional virtual crystal approximation for the SiGe unit cell structure that assumes fixed tetrahedral bond angles and a linear dependence of averaged bond distances ($R_{Si-Si} = R_{Ge-Si} = R_{Ge-Ge}$) on composition $x$ [7]. It has long been recognized that there exist two main local strain release modes, i.e., radical bond-distance change and tetrahedral bond-angle distortion, which should be responsible for the above abnormal behaviors of $Si_{1-x}Ge_x$ alloys. However, many scientific papers are still published concerning which are the most important modes and how the abnormal behaviors are caused [10–14], implying a lack of a full understanding of the underlying physics.

Whilst most theoretical efforts are concentrated upon the variations of the NN bond distances and bond angles with $x$ [10–12], experimental studies by using extended x-ray absorption fine structure (EXAFS) spectroscopy are usually limited to the NN bond distances because bond angles are difficult to measure [7,15,16]. Nevertheless, the qualitative modifications of higher NN bond distances provide an indirect way to infer the roles of different lattice relaxation modes. In particular, when compared to the Si–Si second NN bond distance in bulk Si, the stretching of Ge–Si second

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* Corresponding author.
*E-mail address:* chendl@ihep.ac.cn (D. Chen).

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NN bond distance would be dominated by the elongation of Ge–Si first NN bond distance, whereas the contracted Ge–Si second NN bond distance implies overwhelming Ge–Si–Si tetrahedral angle distortion. Interestingly, despite the extensive studies, controversial issues still exist regarding the qualitative change of the second NN bond distance in the literature. Matsuura et al. measured the Ge–Si NN bond distances using Ge *K*-edge EXAFS for strained $Si_{1-x}Ge_x$/Si(100) epitaxial films with $x$ ranging from 0.06 to 0.18 [15]. Without any dependence of Ge concentration, the Ge–Si second NN bond distance was shown to be about 0.01 Å larger than the second NN Si–Si bond distance in bulk Si. Subsequently, Woicik et al. measured the local structure within strained $Si_{1-x}Ge_x$ layers ($x$~0.22) on Si(001) by polarization-dependent Ge *K*-edge EXAFS [16]. However, the Ge–Si second NN bond distance was shown to be compressed by about 0.01 Å. Recently, Sun et al. studied the local lattice distortion in Ge-dilute $Si_{1-x}Ge_x$/Si(100) epitaxial film ($x$~0.006) as a function of temperature using Ge *K*-edge EXAFS multiple-scattering (MS) analysis [14]. Also, they confirmed a contracted Ge–Si second NN bond distance and ascribed it to the negative deviation of the Ge–Si–Si tetrahedral bond angle. On the other hand, although also exhibiting negatively deviated Ge–Si–Si tetrahedral bond angle when $x < 0.5$ in relaxed $Si_{1-x}Ge_x$ alloys, many theoretical calculations predicted a general stretching trend for the Ge–Si second NN bond distance [10,11,17,18]. Those results suggest that the substrate effect on local lattice distortion in strained $Si_{1-x}Ge_x$ alloys still remains unclear and the key to resolve the discrepancies would depend critically upon the accurate measurement of the NN bond distances that could be compressed by the residual stress exerted by the Si substrate. For EXAFS, to properly determine the local structural distortion relies upon reliable expression for the interatomic distributions. The anharmonicity of bond-distance distributions has been shown to be prominent in many ionic binary systems such as alkali halides and to usually contribute an additional shift to the harmonic bond distances [19], but for covalent $Si_{1-x}Ge_x$ alloys EXAFS results concerning anharmonicity can hardly be found in the literature. This status raises several questions: Is the anharmonic effect important in $Si_{1-x}Ge_x$ alloys? How does the local structure achieve strain accommodation under anharmonic bond distributions?

In this paper, we present detailed study of the Ge *K*-edge EXAFS spectra of strained Ge-dilute $Si_{1-x}Ge_x$ alloy using advanced data-analysis technique (GNXAS [20,21]) and *ab initio* molecular dynamics (AIMD) simulations. Ge-dilute $Si_{1-x}Ge_x$ alloy is chose owing to its intrinsic simplicity such as pure Ge–Si coordination as well as low structural disorder which could ensure an accurate measurement of the thermal anharmonic effect and local lattice distortion around Ge. For the first time, prominent deviation from the harmonic approximation is observed for the Ge–Si first NN distribution, and its influences on local lattice distortion and on estimation of the dominant strain release mechanism are also discussed.

## 2. Experimental and computational details

The strained $Si_{0.99}Ge_{0.01}$ alloy film was grown by molecular-beam-epitaxy (MBE) according to Ref. 7. The 1% Ge composition was chosen to ensure both good signal-to-noise ratio (SNR) for EXAFS measurement and avoidance of possible Ge–Ge correlations such as Ge-dimer, Ge-trimer, or Ge cluster. The sample was deposited on commercial Si(100) wafer with a typical growth temperature of 500 °C and a base chamber pressure of $1{*}10^{-10}$ mbar. The desired composition was achieved by adjusting source fluxes, with a final thickness of 200 nm. The Ge *K*-edge EXAFS spectrum of as-prepared sample was acquired at 1W1B beamline of Beijing Synchrotron Radiation Facility (BSRF) in China in fluorescence mode using a Si(111) double crystal monochromator under ambient condition. The incident and fluorescence x-ray intensities were detected using ionization chamber filled with 25% Ar and 75% $N_2$ and Lytle-type detector filled with pure Ar, respectively.

AIMD simulations were performed to examine the thermal effect on bond-distance distributions using the Vienna *ab initio* simulation package (VASP) [22], with pseudopotentials of the projector-augmented wave (PAW) basis set type [23]. Exchange-correlation potentials were described by local density approximation functional [24]. The electronic orbitals were expanded in plane waves with an energy cutoff of 300 eV and $2 \times 2 \times 2$ Γ-centered *k*-meshes were used for BZ sampling, to achieve the force convergence of less than 1 meV/Å. Periodic boundary condition was adopted to calculate the Hellmann-Feynman forces acting on atoms. The time step was 1fs. The system was well-equilibrated at 300 K with a Nosé-thermostat for 20 ps using canonical (NVT) ensemble, the last 16 ps being used to take temporal averages. The simulations were performed starting from a diamond-structured $2 \times 2 \times 2$ supercell of $Si_{63}Ge_1$ containing one substitutional Ge and 63 Si atoms with $x$~0.016 (comparable to the grown sample composition), accompanied by a parallel calculation of pure Si ($Si_{64}$) for comparison. The volumes were chose to correspond to the experimental density [25].

## 3. Date analysis and results

Experimental results regarding the bond-angle changes in $Si_{1-x}Ge_x$ alloys had been scarcely reported in the literature. Here we carried out EXAFS data-analysis for the strained $Si_{0.99}Ge_{0.01}$ sample within the framework of the GNXAS package [20,21], by which both bond distances and bond angles can be obtained simultaneously. A cluster was constructed with the phase shift for each nonequivalent atomic site calculated using the Hedin-Lundqvist approximation for the exchange-correlation part of the optical potential. We limited present analysis to the third NN shell frequency range, and therefore it included the following components: (a) Ge–Si1 first, Ge–Si2 second, and Ge–Si3 third NN shells at distances $R_1$, $R_2$, and $R_3$ contributing the two-body signal $\gamma_1^{(2)}$, $\gamma_2^{(2)}$, and $\gamma_3^{(2)}$ with degeneracy of 6, 12, 12, respectively; (b) Si1–Ge–Si1 triangular arrangement involving two Ge–Si1 bonds which form the intra-tetrahedral angle $\theta_1$ and giving rise to the three body signal $\gamma_1^{(3)}$ with degeneracy of 6; (c) Si1–Ge–Si2 triangular arrangement described by Ge–Si1 bond, Ge–Si2 bond, and bond angle $\theta_2$, which contributes the three body signal $\gamma_2^{(3)}$ with degeneracy of 12. To take into account the anharmonic effect, a Γ-like function [19] was used for the Ge–Si first and second NN distributions, with the dimensionless skewness parameter $\beta$ being indicative of the asymmetry. Other distributions were approximated by Gaussian function. All signals were calculated by continued-fraction algorithm. The opening of 1*s*–3*d* and 1*s*–3*p* double-electron excitation channels for Ge occurring at about 40 and 140 eV above the absorption edge were accounted for using empirical functional model [26]. The overall amplitude correction factor ($S_0^2$) was fixed to be 0.87 and the zero of the theoretical energy scale ($E_{0T}$) was tuned to be 4.4 eV above the Ge *K*-edge.

Fig. 1 shows the best-fit EXAFS signals in *k*- and *R*-spaces. The *k*-range of 3.2–14.7 $Å^{-1}$ and the average SNR are considerably enhanced over previous measurements. While the Ge–Si1 shell contributes the dominant structural signal, the two three-body signals provide detectable contributions and cannot be neglected (see Fig. 1(a) and (b)). Interestingly, $\gamma_2^{(3)}$ is nearly of opposite phase to $\gamma_2^{(2)}$ in low-*k* range and contributes a double peak spreading from 2.4 to 4.5 Å in *R*-space that overlaps significantly with the two single peaks of $\gamma_2^{(2)}$ and $\gamma_3^{(2)}$, emphasizing the importance of $\gamma_2^{(3)}$ in the accurate fitting process. The total theoretical signal in *k*-space