

Local Lattice Distortion of Ge Impurity in Si (001): Multiple-Scattering EXAFS Study

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Abstract. The local structure of dilute Ge impurity in the Si host has been studied by fluorescence x-ray absorption fine structure spectra through multiple-scattering data analysis method. Contrary to the elongation of 0.029 Å for the Ge-Si distance in the first shell, the Ge-Si interatomic distance in the second shell shows a contraction of about 0.013 Å relative to the corresponding Si-Si distance in the Si host. This coincides with the theoretical prediction by Mousseau and Thorpe [Phys. Rev. B 46, 15887 (1992)] which includes both the bond length mismatch and bond-angle deviation. It turns out that the contraction of the second-shell Ge-Si distance is due to the deviation of Ge-Si-Si bond-angle from the ideal tetrahedral angle. From the Ge-Si distances within the first three shells, it is revealed that the dilute Ge doped into Si host can lead to the local distortion rather than the average lattice change.

Keywords: MS-EXAFS, local structure, $\text{Ge}_{0.006}\text{Si}_{0.994}$ thin film.

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INTRODUCTION

It has long been known that nonlinear variation of the band gap of the $\text{Ge}_x\text{Si}_{1-x}$ alloys with composition is associated with the displacement of the microscopic atomic structure from ideal lattice sites [1] which were often assumed in terms of a virtual crystal approximation (VCA) [2]. Therefore understanding the local structure of $\text{Ge}_x\text{Si}_{1-x}$ alloys is essential to precisely calculate their band structures. A lot of experimental [3] and theoretical [4-7] works have been done to investigate the composition dependence of the bond lengths; unfortunately, some discrepancy still exists.

Most of the experimental investigations on $\text{Ge}_x\text{Si}_{1-x}$ alloys by using extended x-ray absorption fine structure (EXAFS) mainly focus on the variation of Ge-Si and Ge-Ge bond lengths with x . Few results regarding $\text{Ge}_x\text{Si}_{1-x}$ alloys in the dilute limit ($x \sim 0$) can be found in literature. The $\text{Ge}_x\text{Si}_{1-x}$ alloys of dilute Ge content can provide a good opportunity to investigate the lattice distortion around Ge atoms in the Si host and to test the validity of theoretical calculations in the limit cases. It is also expected that the Ge-dilute Ge-Si alloys are favorable to address the effects of Coulomb forces [8].

In this paper, multiple-scattering (MS) EXAFS analysis is performed to study the local structures

around Ge atoms up to the third shell for the $\text{Ge}_x\text{Si}_{1-x}$ alloy in the dilute Ge limit ($x=0.006$). We aim to investigate the local lattice distortion including both bond length and bond angle variations induced by the dilute Ge impurity.

EXPERIMENT

The 2 μm-thick $\text{Ge}_{0.006}\text{Si}_{0.994}$ thin film sample was prepared by molecular beam epitaxy (MBE), which was described elsewhere [9]. XAFS measurements were performed at BL-13B of the Photon Factory of National Laboratory for High Energy Physics (PF, KEK). The electron beam energy was 2.5 GeV and the maximum stored current was 400 mA. The Ge K-edge XAFS spectra of the $\text{Ge}_{0.006}\text{Si}_{0.994}$ thin film were recorded in a fluorescence mode by using a 19-element pure Ge solid-state detector. Three independent XAFS measurements were carried out at different temperatures of 20, 100 and 300 K, especially, at low temperatures to minimize thermal disorder. EXAFS data were analyzed by using the USTC-XAFS3.0 software package [10] according to the standard procedures.

RESULTS AND DISCUSSIONS

Figure 1 shows the Ge K-edge EXAFS function $\chi(k)$ of the $\text{Ge}_{0.006}\text{Si}_{0.994}$ thin film. All the $\chi(k)$

functions exhibit strong oscillations in the low k region with the maximum at about $k=4 \text{ \AA}^{-1}$, then decrease sharply with the increase of k . This characteristic indicates that the Ge atoms in the $\text{Ge}_{0.006}\text{Si}_{0.994}$ thin film are predominantly surrounded by the light element Si. The solid lines in Fig. 2 show the radial structural functions (RSF) of the $\text{Ge}_{0.006}\text{Si}_{0.994}$ thin film obtained from Fourier transforming the $k^2\chi(k)$ spectra. The strong high shell peaks allow us to perform a MS analysis on the local structure beyond the first shell around Ge atoms.

The least-squares curve fit including the MS contributions was performed by using the FEFFIT code of UWXAFS3.0 package [11]. The theoretical scattering amplitude and phase-shift functions of all the single-scattering (SS) and MS paths were calculated by FEFF7 [12]. From our previous results on the MS effects in zinc-blende structures [13], we only considered three SS paths plus one dominant triangular double-scattering path for analyzing the local structures within the first three shells.

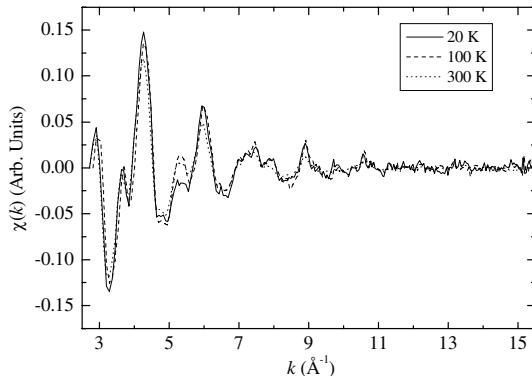


FIGURE 1. Ge K-edge EXAFS oscillation function $k^2\chi(k)$ for $\text{Ge}_{0.006}\text{Si}_{0.994}$ thin film recorded at 20, 100 and 300 K.

In the fitting procedure the coordination number was fixed to the nominal value for each scattering path. We analyzed the data in two steps. First, a single-shell fit for the nearest Ge-Si coordination was done in the R -range [1.2, 2.5] \AA . Second, in the MS fits for higher shells in the R -range [2.5, 4.8] \AA , the shift of the energy origin ΔE_0 was fixed to the best-fit value for the first-shell to reduce the correlations between interatomic distances R and ΔE_0 . This approximation is reasonable, since Ge and Si are isovalent atoms having very close values of electronegativity. Therefore the electrostatic potentials induced by charge transfer between Ge and Si atoms can be neglected, and the approximation of neutral absorber atom assumed by FEFF7 is valid. The overall fitting results are shown in Figure 2 as circles, and the best-fit structural parameters are summarized in Table 1. The error bars are estimated from the square root of the diagonal elements of the correlation matrix, consistent with the criteria adopted by the International XAFS

Society [14]. In order to compare Ge-Si interatomic distances at different temperatures, we corrected the distances at lower temperatures to the values at room temperature by approximating the thermal expansion coefficient of Ge-Si bonds to be the averaged value of Ge and Si crystals, namely, $4.3 \times 10^{-6} \text{ K}^{-1}$. The corrected $R_{\text{Ge-Si}}$ values, denoted as R^{rt} , are included in Table I.

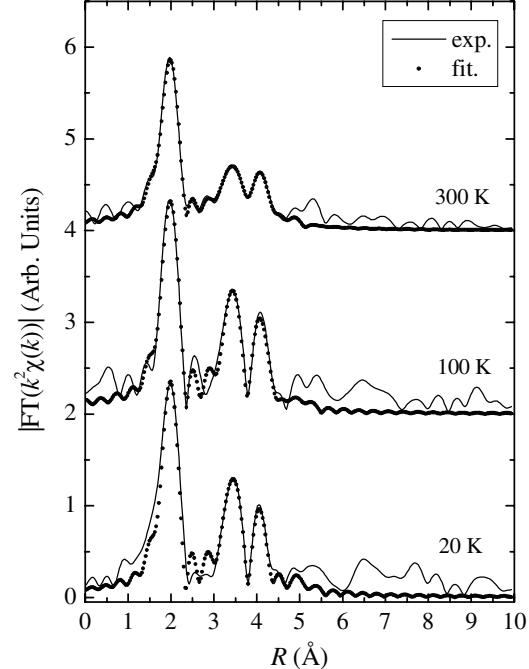


FIGURE 2. The radial structural function by Fourier transforming $k^2\chi(k)$ for $\text{Ge}_{0.006}\text{Si}_{0.994}$ thin film recorded at 20, 100 and 300 K: experimental (solid line) and fitting (circles).

Table I indicates that the averaged Ge-Si bond length of the first shell for the $\text{Ge}_{0.006}\text{Si}_{0.994}$ alloy is 2.381 \AA at 300 K, larger than the Si-Si bond length 2.352 \AA in crystalline Si by 0.029 \AA . However, the Ge-Si distance in the second shell is slightly contracted relative to the Si-Si distance 3.841 \AA . For checking the repeatability of this result we measured the XAFS spectra at different temperatures, especially at low temperatures. Three independent measurements yield the room-temperature Ge-Si distances in the second shell to be 3.828 , 3.831 and 3.835 \AA , respectively, uniformly shorter than 3.841 \AA . The accuracy in determination of the Ge-Si distance is 0.012 \AA , better than the commonly accepted EXAFS accuracy of 0.02 \AA , due to the high signal-to-noise ratio of the EXAFS spectra and the refined data analysis procedure. In fact, the highest accuracy in distance by EXAFS reported in literature can be as high as 0.002 \AA for the first shell [15], and 0.006 \AA for higher shells [16, 17].

TABLE 1. The structural parameters of crystalline Si and Ge_{0.006}Si_{0.994} samples at different temperatures. The underlined values are fixed in the fits. The R^{rt} in the last column is the interatomic distance at room temperature after correcting the thermal expansion effect.

Sample	shell	R (Å)	σ^2 (10 ⁻³ Å)	ΔE_0 (eV)	R^{rt} (Å)
Ge _{0.006} Si _{0.994} (20 K)	1	2.378±0.008	1.8±0.9	8.7±1.0	2.381
	2	3.823±0.012	3.7±1.5	<u>8.7</u>	3.828
	3	4.489±0.030	4.6 <u>±4.3</u>	<u>8.7</u>	4.495
Ge _{0.006} Si _{0.994} (100 K)	1	2.376±0.008	2.0±0.6	8.7±1.0	2.378
	2	3.828±0.012	4.0±1.0	<u>8.7</u>	3.831
	3	4.486±0.030	4.9±1.8	<u>8.7</u>	4.490
Ge _{0.006} Si _{0.994} (300 K)	1	2.384±0.008	4.0±0.5	8.4±0.8	2.384
	2	3.835±0.012	9.6±1.1	<u>8.4</u>	3.835
	3	4.490±0.030	10.8±1.7	<u>8.4</u>	4.490
Crystalline Si	1	2.352			
	2	3.841			
	3	4.504			

Mousseau and Thorpe proposed an analytic calculation for the second nearest Ge-Si distance

$$R_2^{\text{GeSiSi}} = \sqrt{\frac{8}{3}}[(1-x)R_0^{\text{Si-Si}} + xR_0^{\text{Ge-Ge}}] e^{-\frac{1}{8}(\Delta\theta)^2} \frac{\sin \frac{\langle\theta_{\text{Ge-Si-Si}}\rangle}{2}}{\sin \frac{\theta_0}{2}} - \frac{1}{2} a^{**} (R_0^{\text{Ge-Ge}} - R_0^{\text{Si-Si}}) [\sqrt{\frac{8}{3}}x + \sqrt{\frac{3}{8}}(x - \frac{1}{2})]. \quad (1)$$

Here $R_0^{\text{Si-Si}}$ and $R_0^{\text{Ge-Ge}}$ are the Si-Si and Ge-Ge bond length in bulk Si and Ge, $\langle\theta_{\text{Ge-Si-Si}}\rangle$ is the Ge-Si-Si bond angle and $\langle\Delta\theta\rangle$ its standard deviation, $\theta_0=109.47^\circ$, and $a^{**}\approx 0.7$ is the topological rigidity parameter

The $\langle\Delta\theta\rangle$ in Eq. (1) can be evaluated through the total standard deviation $\langle\Delta\theta\rangle_{\text{total}}$ of the Ge-Si-Si bond angle, which consists of configurational and thermal disorder. Following Baker *et al.*, [18] $\langle\Delta\theta\rangle_{\text{total}}$ can be estimated from the Debye-Waller factors σ_1^2 , σ_2^2 of the first and second Ge-Si pairs, which yields $\langle\Delta\theta\rangle_{\text{total}}=3.4^\circ$, 3.5° and 5.0° at 20, 100 and 300 K, respectively. The $\langle\Delta\theta\rangle$ is only the configurational part of $\langle\Delta\theta\rangle_{\text{total}}$, then it is smaller than 3.4° , and $e^{-\frac{1}{8}(\Delta\theta)^2} > e^{-\frac{1}{8}(3.4\pi/180)^2} = 0.9996$. This indicates that it is accurate enough to approximate $e^{-\frac{1}{8}(\Delta\theta)^2} \sim 1$. The bond angle $\langle\theta_{\text{Ge-Si-Si}}\rangle$ in crystalline Ge_xSi_{1-x} alloys has been theoretically calculated by Yu *et al.* [6] and Tzoumanekas *et al.*, [7] who reported $\langle\theta_{\text{Ge-Si-Si}}\rangle=108.7^\circ$ in the $x\sim 0$ limit. Substituting this result into Eq. (1) we get $R_2^{\text{GeSiSi}}=3.834$ Å, which is *shorter* than the expected value 3.841 Å and is in excellent agreement with our averaged experimental result 3.831 Å.

It also need be pointed out that the distance change of the second and third shell with regard to the corresponding Si-Si distance is only at the level of 0.01 Å, obviously less than the change of 0.029 Å in the first shell. This indicates that the position displacement of Si neighbors around Ge atoms is much more significant in the first shell than in the higher shells. Doping Ge into Si host introduces local distortion rather than the average lattice change.

R_2^{GeSiSi} , by taking into account both the bond length mismatch and angular deviation, [5]

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REFERENCES

1. A. Zunger and J. E. Jaffe, *Phys. Rev. Lett.* 51, 662 (1983).
2. R. Bisaro, P. Merenda, and T. P. Pearsall, *Appl. Phys. Lett.* 34, 4457 (1979).
3. See, for example, *Surf. Sci. Rep.* 53, 1 (2004) and references therein.
4. J. L. Martins and A. Zunger, *Phys. Rev. B* 30, 6217 (1984).
5. N. Mousseau and M. F. Thorpe, *Phys. Rev. B* 46, 15887 (1992).
6. M. Yu, *et al.*, *Phys. Rev. B* 64, 165205 (2001).
7. C. Tzoumanekas and P. C. Kelires, *Phys. Rev. B* 66, 195209 (2002).
8. J. C. Woicik, *et al.*, *Phys. Rev. B* 57, 14592 (1998).
9. S. Q. Wei, *et al.*, *J. Appl. Phys.* 82, 4810 (1997).
10. W. Zhong and S. Wei, *J. Univ. Sci. Techn. China* 31, 328 (2001).
11. E. A. Stern, *et al.*, *Physica B* 208&209, 117 (1995).
12. J. Mustre de Leon, *et al.*, *Phys. Rev. B* 44, 4146 (1991).
13. S. Q. Wei and Z. H. Sun, *J. Phys.: Condens. Matt.* 17, 8017 (2005).
14. F. W. Lytle, *et al.*, *Physica B* 158, 701 (1989).
15. Y. Kuwahara, *et al.*, *J. Appl. Phys.* 82, 214 (1997).
16. S. Pasquarelli, *et al.*, *Phys. Rev. B* 56, 1936 (1997).
17. M. Tormen, *et al.*, *Phys. Rev. B* 63, 115326 (2001).
18. S. H. Baker, *et al.*, *J. Phys.: Condens. Matter* 5, 519 (1993).