

## Bond lengths in $\text{Ge}_{1-x}\text{Si}_x$ crystalline alloys grown by the Czochralski method

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(Received 26 March 2001; published 31 August 2001)

We measured the effect of alloy composition on the atomic bonding in bulk  $\text{Ge}_{1-x}\text{Si}_x$  alloys grown by the Czochralski method across the whole composition range  $0 < x < 1$ . Extended x-ray-absorption fine-structure measurements performed at the Ge  $K$  edge at 20 K found that the Ge-Ge and Ge-Si bond lengths maintain distinctly different lengths and vary linearly with alloy composition. The topological rigidity parameter, estimated from the measured bond lengths, is around 0.6, which indicates that the bond lengths and bond angles are distorted with alloy composition.

DOI: 10.1103/PhysRevB.64.113206

PACS number(s): 61.10.Ht, 61.66.Dk

Germanium silicon ( $\text{Ge}_{1-x}\text{Si}_x$  or silicon germanium  $\text{Si}_x\text{Ge}_{1-x}$ , where  $x$  indicates the mole fraction of silicon) alloy is a fully miscible solid solution of the diamond base. The 4.2% difference in the lattice constants of the constituent Ge and Si atoms leads to various unique alloying effects on the electronic, optical, and mechanical properties. Thus, GeSi alloys are important microelectronic and optoelectronic materials in view of the possibilities of band-gap engineering. Knowing the accurate local atomic structure in the context of the local strain relaxation is essentially important in order to clarify the origins of such properties and to develop the device potential of GeSi. Indeed, up to now, much extended x-ray-absorption fine-structure (XAFS) spectroscopy work has been performed to determine bond lengths for different types of neighbor atoms and the corresponding fractional occupancy of each type of neighbor. Unfortunately, despite these studies, e.g., Refs. 1–6, there remains a controversy whether or not the bond lengths vary with composition within GeSi: the so-called Pauling limit<sup>7</sup> or Vegard limit.<sup>8</sup> Indeed, the local structure of GeSi crystal is still in question in relation to theoretical band-structure calculation, such as the virtual-crystal approximation. The GeSi alloys used for these studies were grown as thin films on Si substrates by various epitaxial techniques. However, the large biaxial stress inherent in such heterostructures, even when relaxed through the induction of dislocations, hinders the quantitative study of the native properties of material.

Accordingly, this paper reports XAFS investigations on the bond length of the nearest-neighbor Ge-Ge and Ge-Si atom pair in bulk GeSi crystals grown by the Czochralski method across the whole composition range.

High-quality bulk crystals of  $\text{Ge}_{1-x}\text{Si}_x$  alloys across the whole composition range  $0 < x < 1$  were grown by the Czochralski technique at very low pulling rates ranging from 1 to 8 mm/h in a flowing Ar-gas atmosphere.<sup>9–12</sup> Samples for XAFS measurements were prepared from both grown single crystals of GeSi alloy in the composition ranges  $0 < x < 0.15$  and  $0.85 < x < 1$  and polycrystals in the composition range  $0.15 < x < 0.85$ . The composition of the alloy was determined by means of energy-dispersive x-ray analysis. The ground samples were mixed with BN powders and adjusted the effective thickness to keep the edge jump  $\Delta\mu t \approx 1$ .

X-ray-absorption measurements were conducted by utilizing an XAFS station BL 10B in the photon factory at the High Energy Acceleration Research Organization (KEK), Tsukuba. The storage ring energy was 2.5 GeV and the positron current was 250–350 mA during measurement. A Si(111) double-crystal monochromator was used to define the x-ray energy.<sup>13</sup>  $K$ -edge XAFS of the GeSi alloys were measured in transmission mode at 20 K together with a comparison of that for pure-Ge single crystal. The incident and transmitted x-ray intensities were monitored simultaneously by two ionization chambers. For quantitative EXAFS-data analysis, the parameters of phase shift, amplitude, and electron mean-free path for Ge-Ge and Ge-Si were calculated using the *ab initio* FEFF 6.01 program.<sup>14</sup>

Obtained EXAFS data in the photoelectron wave number  $k$ -range of 0.3–1.69  $\text{nm}^{-1}$  were analyzed for Fourier transfer. Figure 1 shows absolute values of the Fourier transform  $|F(r)|$  of the Ge  $K$ -edge  $k^3\chi(k)$  at 20 K as a function of Si content  $x$  for the  $\text{Ge}_{1-x}\text{Si}_x$  alloys. The intensity of the main peak around  $r = 2 \text{ \AA}$ , which is due to nearest-neighbor atoms around Ge, decreases and becomes asymmetric with decreasing Ge content. In addition, the peak position is also short-

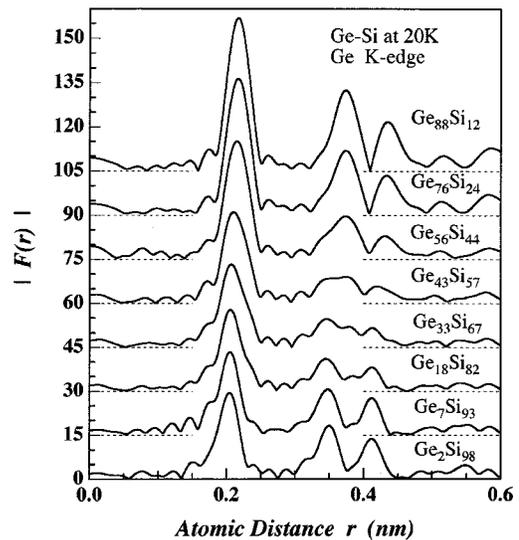


FIG. 1. The absolute values of the Fourier transform  $|F(r)|$  for the Ge  $K$ -edge  $k^3\chi(k)$  of GeSi for various Si content at 20 K.

TABLE I. Structural parameters of GeSi alloys and pure Ge obtained from first peak XAFS data using FEFF 6.01.

Sample (% Si)	Ge-Ge				Ge-Si			
	$N$	$R$ (Å)	$\Delta E$ (eV)	$\sigma$ (Å)	$N$	$R$ (Å)	$\Delta E$ (eV)	$\sigma$ (Å)
0	4.0	2.449	1.4	0.06				
12	3.5	2.441	3.4	0.05				
24	3.1	2.440	2.5	0.05				
44	2.8	2.439	4.4	0.05	1.5	2.405	4.4	0.06
57	1.9	2.425	1.9	0.05	2.2	2.409	5.0	0.05
67	1.6	2.424	1.9	0.05	3.0	2.403	4.4	0.05
82	0.9	2.427	5.0	0.05	3.6	2.395	5.6	0.05
93					4.0	2.385	6.0	0.05
98					4.4	2.385	5.3	0.05

ened. The well-defined double peaks in the higher shells between 3–5 Å can be observed only in the alloys of composition  $x < 0.18$  and  $x > 0.56$ . These features seem to show qualitatively the random-substitution character of the structure, i.e., closer to the Pauling limit<sup>7</sup> than the Vegard limit.<sup>8</sup> The structural parameters around Ge atoms were determined by curve-fitting procedure in the  $k$  space for the first peak of the  $F(r)$  between 0.13 to 0.29 nm. The  $S_0^2$  value was fixed to 1. The results of the quantitative analysis are shown in Table I.

The first-shell Ge and Si coordination numbers around Ge atoms derived from the XAFS data are shown as a function of alloy composition in Fig. 2. The dashed lines show the coordination numbers predicted from a random mixture of Si and Ge atoms. The XAFS results are found to be in good agreement with the random-site occupancy of Si and Ge atoms across the whole composition range.

Diffraction studies of GeSi thin films grown by various epitaxial methods indicate the existence of ordering<sup>15</sup> and Aubry *et al.*<sup>5</sup> pointed out the tendency of clustering of Ge-Ge dimers within Si-rich GeSi thin films. Conversely, there is no report detecting an ordered structure within bulk GeSi crystals.<sup>16</sup> From the present studies, the ordering parameter  $[0.25N_{\text{Ge}} - (1-x)]/(1-x)$  (Ref. 17) estimated from the Ge

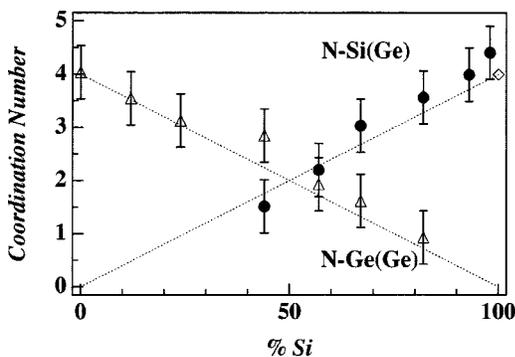


FIG. 2. Ge and Si coordination numbers around Ge atoms derived from XAFS data as a function of Si content. The symbol  $\diamond$  is for pure-Si crystal. The dashed lines show the coordination numbers predicted from a random mixture of Si and Ge atoms.

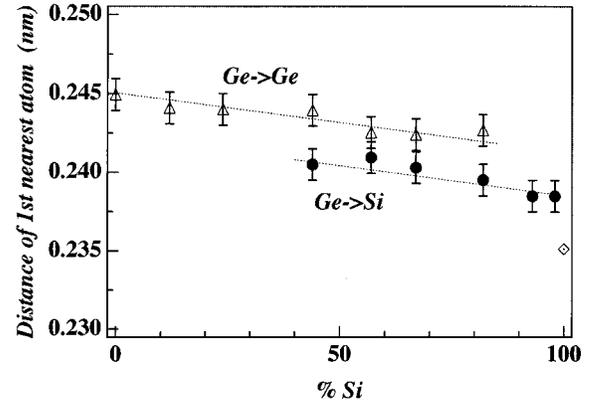


FIG. 3. Ge-Ge bond length and the Ge-Si bond length in GeSi alloys as a function of Si content. The symbol  $\diamond$  shows the bond length of Si-Si in pure-Si crystal. The dashed lines are the predicted compositional dependence of the bond lengths within the topological rigidity model ( $a^{**} = 0.60$ ).

coordination number  $N_{\text{Ge}}$  around the Ge atoms in bulk  $\text{Ge}_{1-x}\text{Si}_x$  crystals ( $0.44 < x < 0.82$ ), is around 0.22–0.29, but not close to 1. Thus, no preferential ordering of the Ge-Ge dimer seems to occur in bulk GeSi crystals across the whole composition range.

Figure 3 plots the experimentally derived Ge-Ge and Ge-Si bond lengths as a function of alloy composition. Although the uncertainty on the derived bond length is less than  $\pm 0.015$  Å, it seems that the Ge-Ge and Ge-Si bond lengths in the GeSi alloys vary linearly and are parallel to each other as a function of Si content. At the composition  $x = 0.5$  the Ge-Si bond length is 2.40–2.41 Å, corresponding to the sum of the Si and Ge covalent radii. Possibly the Si-Si bonds, not investigated in the present study, have the same dependence on composition by analogy with the Ge-Ge and Ge-Si cases.

Our results confirm that the bonding in crystalline GeSi alloys grown by the Czochralski method is closer to the Pauling limit<sup>7</sup> than the Vegard limit,<sup>8</sup> in agreement with most XAFS studies on various semiconductor alloys including GeSi,<sup>1–6</sup>  $\text{Ga}_{1-x}\text{In}_x\text{As}$ ,<sup>18</sup> and  $\text{Zn}_{1-x}\text{Cd}_x\text{Te}$ ,<sup>19</sup> etc. However, the bonds of Ge-Ge, Ge-Si and possibly Si-Si show a dependence of the bonding length on the alloy composition, i.e., they do not follow a strict Pauling model, which is consistent with recent XAFS studies on GeSi alloys.<sup>4,5</sup> The fact that their dependence has the same slope can be explained with regard to the topological rigidity model, similar to the results by Woicik *et al.*<sup>4</sup> but contrary to those by Aubry *et al.*<sup>5</sup>

In the simple model by Cai and Thorpe<sup>20</sup> on the compositional dependence of the first-shell distance in the diamond and relevant structures, a central atom bonded to four neighbor atoms pushes the nearest-neighbor atoms away. The topological rigidity parameter  $a^{**}$ , a measure of the force required to produce unit displacement of the neighbor atoms (Ref. 21), is defined

$$a^{**} = ua/F, \quad (1)$$

where  $F$  is the radial force from the central atom pushing the nearest-neighbor atom away,  $a$  is the radial-force constant for

the bond, and  $u$  is the displacement of the nearest-neighbor atom relative to its natural bond length. A roughly estimated topological rigidity parameter  $a^{**}$  according to the model by Cai and Thorpe<sup>20</sup> is  $0.60 \pm 0.05$ , in agreement with or a little smaller than the values of 0.63–0.70 reported experimentally<sup>3,5</sup> and found theoretically<sup>21</sup> for Ge-Ge bond in GeSi alloys. Since the parameter  $a^{**}$  varies from zero in the Vegard limit to 1 in the Pauling limit, our results mean that both the bond lengths and bond angles are distorted by changes in the composition of GeSi alloys, similar to the reported results for most ternary alloy semiconductors. Typically for  $\text{Ga}_{1-x}\text{In}_x\text{As}$   $a^{**} \approx 0.78$  is estimated from the change of the InAs and GaAs bond lengths across the alloy

composition range.<sup>22</sup> Probably most of the strain in GeSi alloys may be accommodated by changes of both the bond angle and bond length.

In conclusion, we have performed an XFAS study of the local structure of  $\text{Ge}_{1-x}\text{Si}_x$  alloys grown by the Czochralski method in the whole composition range  $0 < x < 1$ . From Ge  $K$ -edge spectra measured at 20 K Ge-Ge and Ge-Si bond lengths have been found to maintain distinctly different lengths and vary linearly with alloy composition and to be close, but not completely, to the Pauling limit. The estimated topological rigidity parameter 0.6 suggests that the bond lengths and bond angles are distorted with alloy composition. It is a task in the future to clarify the compositional dependence of Si-Si bond length in GeSi alloys.

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