

J. Synchrotron Rad. (1999), 6, 790–792

Local structures of $(\text{Ge}_4/\text{Si}_4)_5$ monolayer strained-layer superlattice probed by fluorescence XAFS

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Local structures of $(\text{Ge}_4/\text{Si}_4)_5$ monolayer strained-layer superlattice (MSLS) have been studied by fluorescence XAFS. The distortion of local lattice around Ge atoms is evidenced by the compressed Ge-Ge and Ge-Si bond lengths. $R_{\text{Ge-Ge}}$ (0.243 nm) and $R_{\text{Ge-Si}}$ (0.238 nm) in $(\text{Ge}_4/\text{Si}_4)_5$ MSLS are 0.002 nm shorter than those of c-Ge ($R_{\text{Ge-Ge}}=0.245$ nm) and the sum of covalent radii ($R_{\text{Ge-Si}}=0.240$ nm), respectively. The determined Si coordination number (2.2) is slightly larger than the Ge coordination number (1.8). A simple mechanism of site-exchange between particular sites and the adjacent several layers is proposed to interpret the interface structure for the $(\text{Ge}_4/\text{Si}_4)_5$ MSLS.

Keyword: fluorescence XAFS; Ge_n/Si_n superlattice

1. Introduction

$(\text{Ge}_4/\text{Si}_4)_5$ monolayer strained-layer superlattice (MSLS) grown on Si(001) substrate, possesses the strong optical transitions (0.75, 1.25, 2.31 eV) unique to the superlattice periods, which are found neither in constituent crystals nor in the $\text{Ge}_{0.50}\text{Si}_{0.50}$ alloy (Pearsall *et al.*, 1987). The artificially ordered Ge_n/Si_n small period superlattices have greatly expanded the optical and electrical properties of Ge/Si semiconducting materials, and opened a doorway to band-structure engineering through heterostructures formed from the strained-layer coherent epitaxy of Si and Ge (Bean *et al.*, 1984).

In order to understand the nature of Ge_n/Si_n MSLS quantum well and to achieve significant modifications for the optical and electrical properties, a number of work (Pearsall *et al.*, 1986 and 1992; Ciraci *et al.*, 1988; Wong *et al.*, 1988 and Satpathy *et al.*, 1988) have been performed to study electronic properties, growth, structure and stability of the strained Ge_n/Si_n MSLS and $\text{Ge}_x\text{Si}_{1-x}$ alloys. It is essential to measure the local and interface structure parameters of $(\text{Ge}_n/\text{Si}_n)$ MSLS for quantitative calculations of realistic superlattice band structure and optical transitions.

In this paper, we report the local structures of Ge atoms in $(\text{Ge}_4/\text{Si}_4)_5/\text{Si}(001)$ MSLS probed by grazing-incidence fluorescence XAFS and propose a site exchange model to explain the interface structure.

2. Experimental

$(\text{Ge}_4/\text{Si}_4)_5$ MSLS was prepared on a well-oriented p-type Si(001) substrate in an ultrahigh vacuum molecular beam epitaxy growth chamber. The layer thickness of the Ge_n/Si_n MSLS was analyzed *in situ* by reflection high-energy electron diffraction. The two dimensional growth of Ge and Si layers were performed at 673 K. A typical growth rate are 0.03 nm/sec. and 0.01 nm/sec. for Si and Ge depositions, respectively. The preparation procedure of $\text{Ge}_{0.05}\text{Si}_{0.95}/\text{Si}(001)$ and $\text{Ge}_{0.50}\text{Si}_{0.50}/\text{Si}(001)$ samples is similar to that of $(\text{Ge}_4/\text{Si}_4)_5$ MSLS, using codeposition of stoichiometric element Ge and Si.

The fluorescence yield spectra of Ge samples were measured at the BL-13B of National Laboratory for High Energy Physics (PF, KEK). The electron beam energy was 2.5 GeV. A 27-pole wiggler with the maximum magnetic field B_0 of 1.5 T inserted in the straight section of the storage ring was used. XAFS data were collected using a fixed-exit double-crystal Si(111) monochromator. A 7-element Si(Li) solid-state detector array was used to collect the fluorescence signal. The experiment details have been described elsewhere (Oyanagi *et al.*, 1993). For Ge K-edge fluorescence yield spectra, the large background caused by elastic scattering is eliminated by using the thin Ga X-ray filters for the Ge K-edge. The energy window of the detector electronics for each channel was chosen to record only the $K\alpha$ peaks of Ge element.

3. Results

Figure 1 illustrates the normalized Ge K-edge EXAFS oscillations function $\chi(k)$ in the k range of 20–180 nm^{-1} for c-Ge,

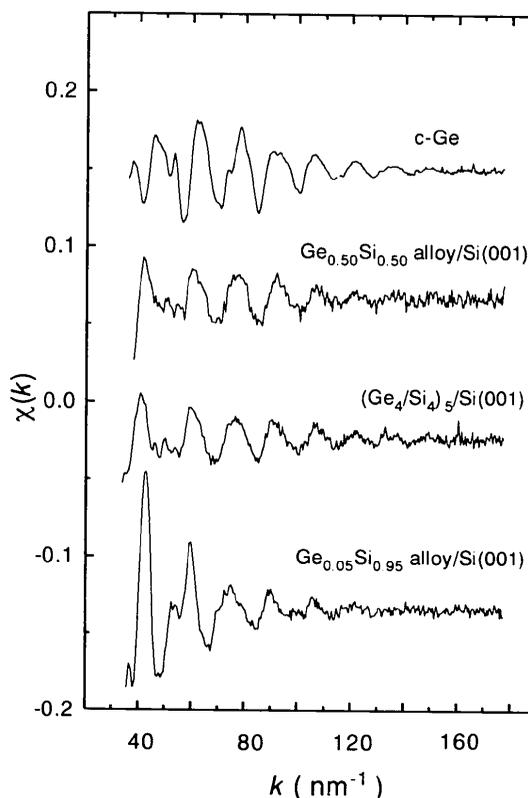


Figure 1

EXAFS oscillation functions $\chi(k)$ for $(\text{Ge}_4/\text{Si}_4)_5/\text{Si}(001)$, $\text{Ge}_x\text{Si}_{1-x}$ alloys and c-Ge (c-Ge data obtained by transmission mode).

$\text{Ge}_x\text{Si}_{1-x}$ alloys and $(\text{Ge}_4/\text{Si}_4)_5$ MSLS. It can be observed that the $\chi(k)$ spectra of $(\text{Ge}_4/\text{Si}_4)_5$ MSLS is strongly different from these of $\text{Ge}_{0.05}\text{Si}_{0.95}/\text{Si}(001)$ and c-Ge, but is similar to that of $\text{Ge}_{0.50}\text{Si}_{0.50}/\text{Si}(001)$.

The results of Fourier transform (FT) of EXAFS oscillations function $\chi(k)$ multiplied by k , representing the radial distribution functions (RDF) are shown in Fig. 2. Compared with c-Ge, the magnitude of prominent peak for $(\text{Ge}_4/\text{Si}_4)_5$ MSLS decreases by about 50% and its position shifts by 0.010 nm toward the smaller distance direction. The results indicate that there exist two closely separated peaks around Ge, which apparently reduce the magnitude of the first nearest peak due to a destructive interference. Such a decrease of intensity is associated with broadening of the peak profile which can be quantitatively analyzed by a least-squares curve fitting analysis. Furthermore, there were no more distinct peaks, due to the second and third

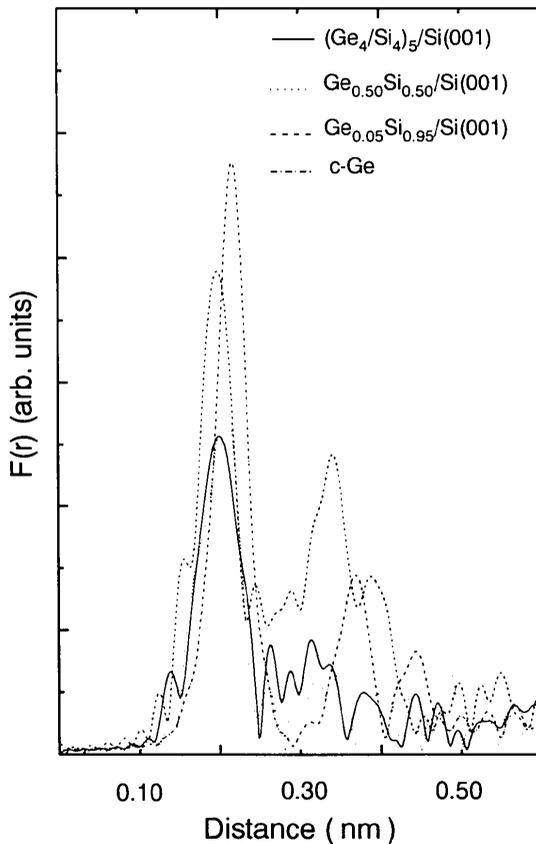


Figure 2
Radial distribution functions obtained by Fourier transform of $k\chi(k)$ for $(\text{Ge}_4/\text{Si}_4)_5/\text{Si}(001)$, $\text{Ge}_x\text{Si}_{1-x}$ alloys and c-Ge.

nearest neighbors in $(\text{Ge}_4/\text{Si}_4)_5$ MSLS. This is also expected for Ge-Si alloys where the second and third shell distances are not unique and the interference reduces the peak intensity. If the superlattice has a medium range order, we would expect higher shells appear as peaks in FT. The least-squares curve fitting was performed to fit the inverse transform of the EXAFS oscillations for the first shell (Sayers & Bunker, 1988). The theoretical amplitude function $|f_i(k, \pi)|$ and phase shift function $F_{ij}(k)$ was obtained by FEFF6 (Rehr *et al.*, 1992). The results of curve

fitting are summarized in Table 1.

Table 1

Structural Parameters obtained from XAFS data for $\text{Ge}_4/\text{Si}_4/\text{Si}(001)$ and $\text{Ge}_x\text{Si}_{1-x}$ alloys

	coordination type	R (nm)	N	sigma (10^{-2} nm)	E(eV)
$(\text{Ge}_4/\text{Si}_4)_5/\text{Si}(001)$	Ge-Ge	0.243 ± 0.001	1.8 ± 0.2	0.56 ± 0.05	7.0 ± 1.0
	Ge-Si	0.238 ± 0.001	2.2 ± 0.2	0.62 ± 0.05	4.0 ± 1.0
$\text{Ge}_{0.50}\text{Si}_{0.50}$ alloy	Ge-Ge	0.242 ± 0.001	2.0 ± 0.2	0.45 ± 0.05	7.0 ± 1.0
	Ge-Si	0.238 ± 0.001	2.0 ± 0.2	0.40 ± 0.05	3.8 ± 1.0
$\text{Ge}_{0.05}\text{Si}_{0.95}$ alloy	Ge-Si	0.235 ± 0.001	4.0 ± 0.2	0.45 ± 0.05	4.5 ± 1.0
c-Ge	Ge-Ge	0.245	4.0	0.58	8.0

4. Discussion

In the previous work (Pearsall *et al.*, 1987 and 1989), we have studied the optical transitions of Ge_n/Si_n ($n=1, 6$) MSLS and $\text{Ge}_x\text{Si}_{1-x}$ alloys with electroreflectance spectroscopy. The results demonstrated that the optical spectra of both $(\text{Ge}_1/\text{Si}_1)_{16}$ and $(\text{Ge}_6/\text{Si}_6)_3$ MSLS are similar to that of $\text{Ge}_{0.50}\text{Si}_{0.50}$ alloy, but the optical spectra of $(\text{Ge}_2/\text{Si}_2)_{10}$ and $(\text{Ge}_4/\text{Si}_4)_5$ show significant departures from that of $\text{Ge}_{0.50}\text{Si}_{0.50}$ alloy. These results indicate that the electronic band structure is strongly dependent on the superlattice period and the local structures difference between $(\text{Ge}_4/\text{Si}_4)_5$ MSLS and $\text{Ge}_{0.50}\text{Si}_{0.50}$ alloy.

People and Jackson have pointed out that the lowest-lying states in the conduction band are derived from the (100) valleys of Si based on an ideal superlattice model (People *et al.*, 1987). However, the magnitude of the calculated matrix elements are several orders lower than what is observed in experiment. On other hand, the calculation taking the realistic structure into account resulted in optical transition matrix elements which are in better agreement with the experimental results (Morrison *et al.*, 1987). Hybertsen *et al.* (1987) has interpreted the strong optical transition (0.75 eV) observed in $(\text{Ge}_4/\text{Si}_4)_5$ MSLS as an indirect transition by local-density-functional and quasiparticle self-energy approach calculation based on an ordered strained-layer superlattice structure with a sharp interface and strain confinement in the Ge layer. Wong *et al.* (1988) have predicted a direct transition by assuming a non-relaxed bulk-bulk Ge-Ge distance (0.245 nm) with pseudopotential calculations. Nevertheless, no real structure parameters have been obtained for the optical calculation for the $(\text{Ge}_4/\text{Si}_4)_5$ MSLS.

The structural parameters in table 1 show that the ratio of Ge and Si coordination number is close to that of $\text{Ge}_{0.50}\text{Si}_{0.50}$ alloy but the Si coordination number is slightly larger for $(\text{Ge}_4/\text{Si}_4)_5$ MSLS. This result reveals that the Ge-Si mixing occurs at the interface. We can estimate a degree of interface mixing based on the fact that the ideally sharp interface should give 1 and 3 for the Si and Ge coordination number as shown in figure 3 (a), respectively. The XAFS studies of Ge epitaxial overlayers upon well-oriented Si(001) ($\text{Ge}_n/\text{Si}(001)$, $n < 7$) (Oyanagi *et al.*, 1995) have indicated that $\sim 1/2$ of Ge atoms in the second layer are replaced by Si atoms in the third layer for 2ML Ge in $\text{Ge}_n/\text{Si}(001)$, relieving elastic strain in the second layer caused by a large atomic size mismatch between the adatom and substrate atoms, in addition to surface rearrangement due to dimers.

We find that the bond lengths $R_{\text{Ge-Ge}}$ (0.243 nm) and $R_{\text{Ge-Si}}$ (0.238 nm) in $(\text{Ge}_4/\text{Si}_4)_5$ MSLS are 0.002 nm shorter than those of c-Ge ($R_{\text{Ge-Ge}}=0.245$ nm) and the sum of covalent radii ($R_{\text{Ge-Si}}=0.240$ nm), respectively. The results imply that the Ge layers in

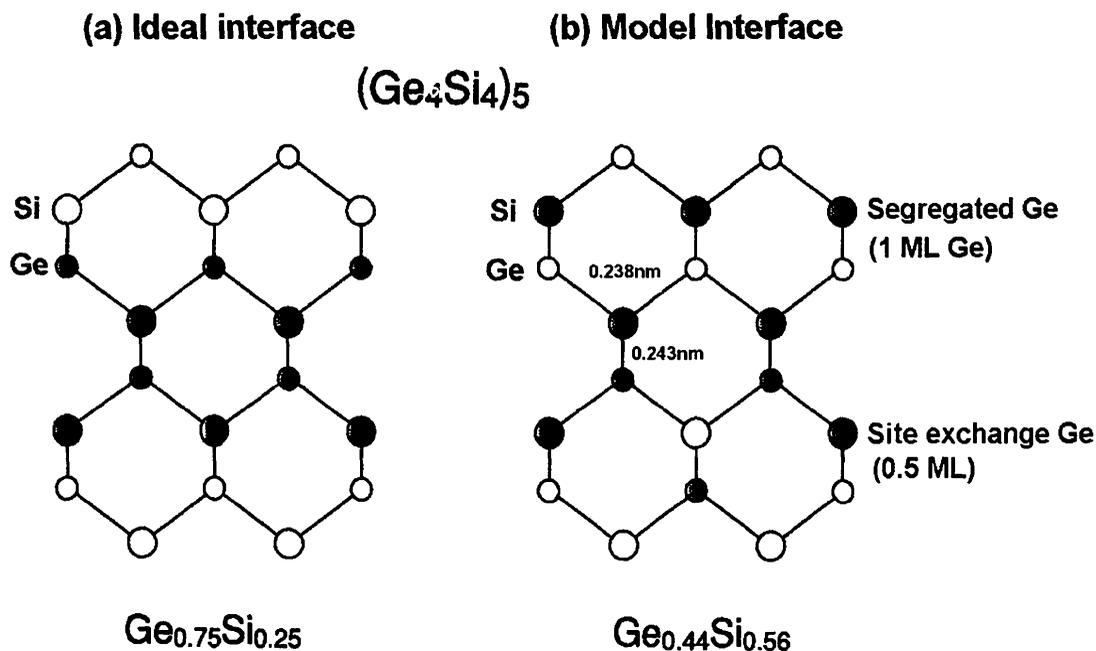


Figure 3

Schematic structure of (Ge₄/Si₄)₅. For ideally sharp Ge/Si interface (a), the average Ge-Si composition is Ge_{0.75}Si_{0.25}. If the half monolayer Ge atoms of the first Ge layer are replaced with Si atoms, and one monolayer Ge atoms in the fourth layer are surface-segregated (model interface (b)), the average composition would be Ge_{0.44}Si_{0.56} which is close to the observed average composition of (Ge₄/Si₄)₅, Ge_{0.45}Si_{0.55}.

(Ge₄/Si₄)₅ MSLS is distorted because of elastic deformation. An interface mixing partially relaxes the strain but the EXAFS results

confirmed that the Ge layer is compressed indicating that the effect of strain should be taken into account in the interpretation of optical properties. A simple model of site-exchange between particular Ge sites and the adjacent Si layer as shown in figure 3 (b) is proposed to explain the Ge-Si interface structure for (Ge₄/Si₄)₅ MSLS. This interface mixing introduces a chemical disorder which consequently induces a structural disorder due to a bond length mismatch between the Ge-Ge and Ge-Si. The symmetry change affects the selection rule of optical excitation. The weak indirect transition is enhanced or, on the contrary, normally inhibited direct transition is allowed. The site exchange is hardly explained in term of thermally activated diffusion. An alternative mechanism of massive interdiffusion is the strain-enhanced surface segregation following subsequent Si deposition on the Ge layer and diffusion at the interface with the Si substrates. Because of a large bond length mismatch (4%) between Ge and Si, tensile sites prefer Ge atoms while compressive sites are stabilized by Si atoms.

5. Conclusion

Fluorescence XAFS have been used to measure the local structures of (Ge₄/Si₄)₅ MSLS. The results show that the distortion of local lattice around Ge atoms is evidenced by the compressed Ge-Ge ($R_{\text{Ge-Ge}}=0.243$ nm) and Ge-Si ($R_{\text{Ge-Si}}=0.238$ nm) bond lengths. The determined Ge/Si coordination number ratio is larger than the ideal value (0.75), indicating a large degree of interface mixing. A model structure based on a site-selective Ge-Si exchange at the interface is shown to explain the EXAFS results.

We express our thanks to Prof. M. Ikeda for useful discussion on the electronic structure. One of authors (S.Q. Wei) thanks the partial support of National Natural Science Foundation of China and returned member of Chinese Science Academy.

References

- Bean, J.C., Feldman, L.C., Fiory, A.T., Nakahara, S. & Robinson, I.K., (1984). *J. Vac. Sci. Technol. A* **2**, 436-440.
- Ciraci, S. & Batra, I.P., (1987). *Phys. Rev. Lett.* **58**, 2114-2117.
- Ciraci, S. & Batra, I.P. (1988). *Phys. Rev. B* **38**, 1835-1848.
- Hybertsen, M.S. & Schluter, M., (1987). *Phys. Rev. B* **36**, 9683-9693.
- Morrison, I., Jaros, M & Wong, K.B., (1987). *Phys. Rev. B* **35**, 9693-9707.
- Oyanagi, H., Sakamoto, K., Shioda, R., Kuwahara, Y., & Haga, K., (1995). *Phys. Rev. B* **52**, 58245829;
- Oyanagi, H., Sakamoto, K. & Sakamoto, T., (1993). *Jpn. J. Appl. Phys.* **32**(suppl), 119-124.
- Pearsall, T.P., Bevk, J., Bean, J.C., Bonar, J., Mannaerts, J.P. & Uurmazd A., (1989). *Phys. Rev. B* **39**, 3741-3757; (1992). *Appl. Phys. Lett.* **60**, 1712-1714.
- Pearsall, T.P., Bevk, J., Feldman, L.C., Bonar, J.M., Mannaerts, J.P., & Ourmazd, A., (1987). *Phys. Rev. Lett.* **58**, 729-732.
- Pearsall, T.P., Pollak, F.H., Bean, J.C. & Hull, R., (1986). *Phys. Rev. B* **33**, 6821-6830.
- People R. and Jackson S., (1987). *Phys. Rev. B* **36**, 1310-1313.
- Rehr, J.J., Zabinsky, S.I. & Albers, R.C., (1992). *Phys. Rev. Lett.* **69**, 3397-3400.
- Satpathy, S., Martin, R.M. & Van de Walle, (1988). *Phys. Rev. B* **38**, 13237-13245.
- Sayers D.E. & Bunker B A, (1988). *X-ray Absorption. Principles, Applications, Techniques of EXAFS, SEXAFS and XANES*, p.211-253, edited by Koningsberger, D.C. & Prins R., John Wiley and Sons, Inc.
- Wong, K.B., Jaros, M., Morrison, I. & Hagon, J.P., (1988). *Phys. Rev. Lett.* **60**, 2221-2224.

(Received 10 August 1998; accepted 17 December 1998)