X-ray Fluorescence Holography Study on Si_{1-x}Ge_x Single Crystal

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We measured the X-ray fluorescence holograms of $Si_{0.999}Ge_{0.001}$, $Si_{0.8}Ge_{0.2}$, $Si_{0.5}Ge_{0.5}$, $Si_{0.2}Ge_{0.8}$ and Ge single crystals, and reconstructed the images of second neighbor atoms around Ge. The positional shift of the atomic image across the whole composition range was three times larger than the value predicted from the difference in the lattice constants of pure Si and Ge. We found that imaginary part of the reconstruction strongly affects the positions of the atomic images. Thus, using the negative real parts, the atomic image became sharp and its shift dependent upon Ge composition comes to the reasonable values.

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1. Introduction

Crystalline Si-Ge alloys have much attention in the field of the semiconductor, because it is theoretically predicted that some strained SiGe materials might have a direct band gap and thus exhibit useful optoelectronic properties. It is essential to know their atomic structure, especially a local structure around Ge, in order to understand the origin of such properties and to develop SiGe devices. From X-ray diffraction, its lattice constant linearly changes with Ge concentration according to Vegard's law.¹⁾ On the other hand, local structures around Ge or Si have been studied by the extended X-ray absorption fine structure (EXAFS). The compositional dependence of the first shell homoatomic and heteroatomic bondings in SiGe alloys has been found to be mostly Pauling type.^{2,3)} Local lattice distortion characterized by the bond-length and angle is a key factor for understanding the electro and optical properties of SiGe system. The analysis of the second- or third-shell by the EXAFS is however a difficult task because the second-shell signal is overlapped with the third-shell signal and heavily contaminated by a triangular multiple scattering path.⁴⁾ Quantitative evaluation of local lattice distortion needs accurate structural data about the second neighbor atoms. X-ray fluorescence holography (XFH) has an advantage to their point as well as three dimensional (3D) structural information.

The XFH is a relatively new novel technique for determination of a local structure, since it provides 3D atomic image around a specified element within a radius of 1 nm.^{5–7)} Some applications to dopants,⁸⁾ quasicrystal⁹⁾ and thin films^{10,11)} have been reported. Recent improvement of XFH made it possible to visualize even light atoms such as oxygen.¹²⁾ The full width of half maximum (FWHM) of the atomic images was achieved to be 0.05 nm,¹³⁾ suggesting that we can determine atomic positions within 0.01 nm. Differently from the EXAFS, the XFH is free from the interference of their holographic signals from the second and third neighbor atoms, since these atoms are present at different coordinates in 3D real space. Therefore, this technique has a great potential to evaluate quantitatively the local lattice distortion in the SiGe system.

In this work, we measured X-ray fluorescence holograms

of SiGe single crystals with various alloy composition and reconstructed atomic images around Ge. From these atomic images, the structural variation dependent upon Ge concentration will be discussed.

2. Experiment

The experiment was carried out at beam line BL37XU and BL47XU in the synchrotron radiation facility, SPring-8, Harima, Japan. Electron storage ring current was between 80 and 100 mA during the measurement. Synchrotron radiation from undulator was monochromatized by a Si 111 double crystal monochromator. Bulk $Si_{1-x}Ge_x$ crystals were grown by the Czochralski method, where x is a mole fraction of Ge.^{14,15)} The x values of the prepared samples were 0.001, 0.2, 0.5 and 0.8. A pure Ge single crystal wafer (Furuuchi Kagaku Co. Ltd.) was used as the standard sample. Dimensions of samples were about 5 mm in a diameter and 3 mm in thickness. The XFH apparatus at SPring-8 was used in this experiment.¹⁶⁾ Data were collected in the inverse mode.⁶⁾ Ge K α (9.87 keV) fluorescent X-rays emitted from the samples were analyzed and focused by a cylindrically bent LiF crystal. The focused beams were monitored by an avalanche photodiode. The total X-ray fluorescence was about two million cps at the sample. The fluorescence intensities were measured as a function of azimuthal angle ϕ and polar angle θ_1 . The X-ray exit angle θ_2 was fixed at 45°. Incident X-ray energies were 14.5-17.5 keV with 0.25 keV steps, and total 13 holograms were recorded in each sample. Since an acquisition time of one hologram was 2.5 h, we spent about 160 h for measuring the total 65 holograms for the five samples.

3. Results and Discussion

All hologram patterns show clear X-ray standing wave (XSW) lines caused by Bragg reflections of incident X-rays. Using the XSW lines, hologram data were four-fold symmetrized in order to increase statistical accuracy. Figure 1 shows the hologram pattern of Si_{0.999}Ge_{0.001} at 14.5 keV. The k_x , k_y and k_z in Fig. 1 are axes in the reciprocal lattice and are respectively expressed as $k_x = |k| \cos \phi \cos \theta_1$,



Fig. 1 Hologram of Si_{0.999}Ge_{0.001} taken at X-ray energy of 14.5 keV.

 $k_{v} = |k| \cos \phi \cos \theta_{1}$ and $k_{z} = |k| \sin \theta_{1}$, where k is a wave number of the incident X-rays. Barton's algorithm for multiple energy reconstruction was applied to the processed data.17) The (001), (004), (110) and (100) planes were reconstructed for all samples. All observed atomic images elongate along the *c*-axis due to the limited k_z range of the measured holograms. This problem can be resolved by extending the holograms to 4π sphere.¹³⁾ This technique is, however, very delicate, and the obtained holographic signal will be easily destroyed. Therefore, in this work, we did not adopt this full extension technique. We estimated the positions of atoms from the cross section intensity of the reconstructed images. In this study, atomic distance between the center Ge and atoms on the (001) planes were analyzed by the present method, because it is difficult to determine the accurate distances to the atoms on other planes due to the elongation of the atomic images along *c*-axis.

Figure 2 shows the reconstructed image of the (001) plane for the present samples. Second neighbor $\pm 1/2, \pm 1/2, 0$ atoms are visible for all samples, but intensities of the fourth neighbor $\pm 1, 0, 0$ or $0, \pm 1, 0$ atoms decrease with increase in the Ge concentration. Enlarged views of the second neighbor atoms are shown in Fig. 3. With the increase in the Ge concentration, the atomic position gradually changes from 0.387 nm to 0.439 nm. This result seems to be natural taking into account Vegard's law. Considering that $a/\sqrt{2}$ of the pure Si and Ge are 0.384 and 0.400 nm, respectively, where *a* is lattice constant, we notify that the shift of the atomic images (0.052 nm) is about three times larger than the difference of the $a/\sqrt{2}$ value between Si and Ge (0.016 nm). This clearly indicates that we can not carry out quantitative discussion in the images as they are, although they evidently provide us qualitative structural information. In order to overcome this difficulty, we tested a new analysis to discuss atomic positions in a more quantitative manner. We plotted out the reconstructed intensities of 1/2, 1/2, 0 atoms and their real and imaginary parts in the radial direction for the Si_{0.999}Ge_{0.001} and pure Ge samples, as shown in Figs. 4(a) and (b), respectively. Both the real and imaginary parts oscillate strongly at the atomic images. In principle, the real



Fig. 2 Reconstructed atomic image of (001) plane. (a) $Si_{0.999}Ge_{0.001}$, (b) $Si_{0.8}Ge_{0.2}$, (c) $Si_{0.5}Ge_{0.5}$, (d) $Si_{0.2}Ge_{0.8}$, (e) pure Ge, (d) indication of atoms on (001) plane.

part of reconstruction obtained by the Barton's algorithm shows a negative peak at an atomic position, and the imaginary part is constantly zero. This was confirmed by the computer simulation. In the present reconstructions, it is found that the positions of the atomic images of $Si_{0.999}Ge_{0.001}$ and Ge in Fig. 2 are located at the maximum and minimum values of the imaginary parts, respectively. This means that both the atomic images were strongly affected by the imaginary parts rather than the real. The similar trend was seen in the reconstructions of the other samples of $Si_{0.2}Ge_{0.8}$, $Si_{0.5}Ge_{0.5}$ and $Si_{0.8}Ge_{0.2}$.

Actually, Marchesini *et al.* used the negative real part as atomic image,⁹⁾ and Omori *et al.* displayed the absolute intensity only when the real part was negative.¹⁸⁾ According to Marchesini's work, only the negative real parts for the second neighbor atoms in all samples are shown in Fig. 5. The displayed area is the same as in Fig. 3. It was found that the atomic images in Fig. 5 were remarkably improved. Figure 6 plots the positions of the peak maxima in Fig. 5 as a function of Ge content. The variation of $a/\sqrt{2}$ according to Vegrad's law was added for reference. With increase in the Ge concentration, the peak position shifts from 0.400 to 0.426 nm. This 0.026 nm shift is a half of the value obtained by the absolute intensities, and 0.010 nm larger than the difference between pure Si and Ge. On the assumption that



Fig. 3 Reconstructed images of 1/2,1/2,0 atoms. (a) Si_{0.999}Ge_{0.001}, (b) Si_{0.8}Ge_{0.2}, (c) Si_{0.5}Ge_{0.5}, (d) Si_{0.2}Ge_{0.8}, (e) pure Ge. Break lines at 0.384 and 0.400 nm indicate the distances of $a/\sqrt{2}$ of pure Si and Ge, respectively.



Fig. 4 Plots of reconstructed intensities of 1/2,1/2,0 atoms. (a) Si_{0.999}Ge_{0.001}, (b) pure Ge. Solid lines represent absolute values. Dotted and break lines represent their real and imaginary parts.



Fig. 5 Negative real parts of the reconstructions of 1/2, 1/2, 0 atoms. (a) Si_{0.999}Ge_{0.001}, (b) Si_{0.8}Ge_{0.2}, (c) Si_{0.5}Ge_{0.5}, (d) Si_{0.2}Ge_{0.8}, (e) pure Ge. Break lines at 0.384 and 0.400 nm indicate the distances of $a/\sqrt{2}$ of pure Si and Ge bulks, respectively.

the actual distance to the second neighbor atom in Si_{0.999}Ge_{0.001} is almost equal to that of pure Si (0.384 nm),²⁰⁾ the images of the second neighbor atoms are displaced outward by 0.016 nm from the locations predicted from pure Si, and the displacement becomes larger with increase in the Ge. Len et al. explained the positional shift in the XFH by the slight phase shift of atomic scattering factor as a function of scattering angle.¹⁹⁾ Since the displacements for Si and Ge atoms were roughly estimated to be 0.001 and 0.005 nm, respectively, this will be one reason of the above shift. However, this is not enough to explain the observed shift of 0.016-0.024 nm. Our computer simulation study could not reproduce this phenomenon. An experimental imperfectness, such as limited θ_1 range and/or insufficient pixel number of holograms, is considered as a possible reason.

Figure 6 also plots FWHMs of the peaks for all samples. The FWHMs of the peaks of the $Si_{0.8}Ge_{0.2}$, $Si_{0.5}Ge_{0.5}$ and $Si_{0.2}Ge_{0.8}$ are large compared to those of $Si_{0.5}Ge_{0.5}$ and pure Ge. This reflects the existence of four kinds of bonds, Ge-Si-Si, Ge-Si-Ge, Ge-Ge-Si and Ge-Ge-Ge, around Ge upto the second shell for $Si_{0.8}Ge_{0.2}$, $Si_{0.5}Ge_{0.5}$ and $Si_{0.2}Ge_{0.8}$. The atoms of these configurations appeared at slightly different



Fig. 6 Position (open circle) and FWHM (close circle) of atomic image as a function of Ge content. These values are obtained from the reconstructions in Fig. 5. Break line shows $a/\sqrt{2}$ according to Vegard's rule.

position in the reconstructions, and caused the peak broadening as already shown in Fig. 5. While, the FWHM of the $Si_{0.999}Ge_{0.001}$ is lower than those of above three samples, revealing that Ge-Si-Si bond is dominant. This result is reasonable taking into account the nature of the random substitution in SiGe system³⁾ and the Ge content of this sample.

4. Conclusions

We measured the X-ray fluorescence holograms of the $Si_{1-x}Ge_x$ single crystals grown by the Czochralski method, and analyzed the reconstructed image of the second neighbor atoms around Ge in particular. Its position shift across the composition range 0.001 < x < 1 was three times larger than the value predicted from the lattice constants of pure Si and Ge. This is mainly due to the strong oscillation of the imaginary parts of reconstructions. In order to solve this problem, the atomic images were reconstructed using only the negative real part. The resulted atomic images become sharp and the positional shift becomes a reasonable value. By improving the data processing technique, we will extract more detailed structural parameter about lattice distortion in order to determine the local lattice strain. Further improvement of the XFH analysis will be continuously carried out.

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