1. Introduction

Fluorescent X-rays emitted from an atom in a single crystal are scattered by neighboring atoms and interfere with unscattered fluorescent X-rays. This interference forms a holographic pattern on a sphere around the sample, which can be transformed into three-dimensional atomic images by Fourier transform method. In 1948, the holographic method was first proposed and demonstrated by Gabor in order to improve the spatial resolution of electron microscopy. This technique has been successfully used to image nanometer-scale structures using electrons from field emission tips, but the electron source size had not been small enough to image atomic structures on an angstrom scale. Szöke pointed out that a photoexcited atom within a sample was an ideal source of coherent waves for atomic resolution holography, and proposed the concepts of an X-ray fluorescence holography (XFH) and an X-ray photoemission holography (XPH). XPH is a powerful tool for studying surface structure. Although Barton explained that an atomic image could be obtained from XPH by the Fourier transform method, the image is not clear due to the multiple scattering and phase shift resulting from electron scattering.

Since the effects of phase shift and the multiple scattering of X-rays are negligible in data analysis, X-ray scattering is much more ideal than electron scattering, and X-ray fluorescence holography (XFH) has recently been attracting attention. Independently suggested the possibility of X-ray fluorescence holography based on a similarity between XPH and XFH. Some of the present authors applied for a Grant-in-Aid for Scientific Research from the Ministry of Education and Science, Sports and Culture, in the field of materials science and engineering in 1993, with the same form being resubmitted every year for the subsequent three years. Finally the forth application was accepted in the field of applied analytical chemistry in 1997 and we performed the XFH experiments. The first XFH experiment has been already performed by Tegze and Faigel.

Tegze and Faigel measured the XFH for a strontium titanate (SrTiO3) crystal. The reconstructed image clearly exhibited strontium atoms, though the titanium and oxygen atoms were not observed because these atoms were too light. The disadvantage of XFH was the limited number of characteristic lines of elements present in the sample. This problem has been solved by multiple energy X-ray holography (MEXH), which was based on the idea of the optical reciprocity of XFH and the application of known principles for X-ray standing waves. MEXH allows holograms to be recorded at an arbitrary energy, which can suppress the twin-image effect.

The problem of XFH and MEXH is that the holographic oscillation is feeble in the angular distribution of the fluorescence intensity. Thus, it is difficult to recognize the fine structure of the hologram from the raw data. Many researchers have used the low-pass filters in order to extract hologram from the noisy data, but they did not present details on the numerical procedures in their papers. We have measured the X-ray fluorescence holograms of single crystals and dopants in wafers. Our hologram data were also very noisy, and it was difficult to identify the anisotropy of the intensity in the raw data. In our previous paper, we recorded the X-ray fluorescence hologram of SrTiO3 and found that the smoothing technique was useful in the identification of the holographic oscillation. However, we did not show the reconstructed image. Subsequently, we successfully obtained a clear atomic image of SrTiO3 from the same data. In the present paper, we describe the details of the numerical procedure of obtaining a clear atomic image from the hologram.

2. Experimental

The hologram was measured at the synchrotron bending magnet beam line BL-4A at the Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba, Japan. The current of the electron storage ring was between 400 and 200 mA during the measurements. The SrTiO3 single crystal (001) was purchased from Shinkosha Co. (Tokyo, Japan). The orientation of the single crystal was checked by examining its X-ray Laue pattern. The dimensions of the sample were 10.0 × 10.0 mm2 and 0.5 mm thick. The single crystal was mounted on a rotatable stage to provide rotation of the azimuthal angle, φ.
The value of \( \phi \) was defined as the angle between the [110] direction and the projection of the incident beam. The incident beam size was 1.0 \( \times \) 1.0 mm\(^2\) and the X-ray energy was 16.5 keV, which was just above the Sr K absorption edge. The incident X-ray beam intensity was monitored by an ionization chamber. The X-ray fluorescence exit slit, which allowed the polar angle, was set on a rotatable stage. The angular resolution of the slit was 0.88\(^\circ\). The Si(Li) solid state X-ray detector was used. The details of the experimental setup have been given in ref. 12. The count rate of the Sr K\(\alpha\) X-ray fluorescence was about five thousand counts, and the total integrated intensity of the Sr K\(\alpha\) fluorescence at each pixel was twenty-five thousand counts. One scan was repeated 5 times within the ranges of 35\(^\circ\) \( \leq \theta \leq \) 55\(^\circ\) and -60\(^\circ\) \( \leq \phi \leq \) 60\(^\circ\); the dwelling time for one pixel was 10 s with 5\(^\circ\) steps in \( \theta \) and 1\(^\circ\) steps in \( \phi \). Data from 5 scans were accumulated. The total required time was 9 h.

3. Results and Discussion

The measured Sr K\(\alpha\) X-ray fluorescence intensity was normalized with respect to the incident X-ray intensity, because the incident synchrotron X-ray intensity decayed exponentially during one scan. The normalized fluorescence intensity \( I(\phi, \theta) \) was transformed into \( \chi(\phi, \theta) \) using

\[
\chi(\phi, \theta) = \frac{I(\phi, \theta) - I_0(\theta)}{I_0(\theta)},
\]

where \( I_0(\theta) \) is the average intensity over the whole \( \phi \) scan range. Figure 1 shows \( \chi(\phi, \theta = 45^\circ) \). S/N of the raw data was poor and no anisotropy of fluorescence intensity could be seen because the total count in each pixel (\(~2.5 \times 10^6\) counts) was not enough for observing the fine structure in the raw data. Tegze and Faigel commented that at least \( 4 \times 10^6 \) counts were needed in every pixel, because the calculated value of the anisotropy in the intensity was 0.3\%. On the other hand, this angular distribution of the fluorescence intensity was considered to be included also Kossel lines, because the angular resolution of detecting slit was 0.88\(^\circ\) and step size of \( \Delta \phi \) was 1\(^\circ\). Since strong and sharp peak was observed at \( \phi = 2^\circ \), 22\(^\circ\) in Fig. 1(a), we evaluated the relationship between these peaks and Kossel lines by calculating the \( \phi \) values where the intensive Kossel lines appeared at \( \theta = 45^\circ \). Consequently, any Kossel lines estimated did not exist at around \( \theta = 2^\circ \), while that of 111 reflection existed at \( \theta = 23.3^\circ \), suggesting that the sharp peak at \( \theta = 22^\circ \) was Kossel line.

In order to clarify the fine structure in the angular distribution of X-ray fluorescence intensity, the data were smoothed by the second order Savitzky-Golay method.\(^{21, 22}\) Here, our purpose was to obtain the atomic image of nearest-neighbor Sr atoms, because the total count for each pixel was too low to obtain the atomic image of the second and third neighbor Sr atoms. The average period of holographic oscillation from the nearest Sr atoms was calculated to be about 25\(^\circ\). The effective interval point was 70\% of the full width of half maximum (FWHM) of a peak.\(^{23}\) Since the FWHM of the holographic oscillation was regarded as 12.5\(^\circ\) which was a half of the average period, a smoothing interval of 9 points was chosen. The smoothing used this interval point exclude the holographic oscillation from second and third neighbor Sr atoms. The iteration of smoothing was expected to reveal the structure in the noisy spectrum. Data with smoothing repeated 2, 5 and 50 times are shown in Fig. 1 together with the raw data. The twice smoothed data were still noisy and the fine structure could not be recognized. The 5-times smoothed data clearly show mirror symmetry, and the amplitude of the oscillation was about 0.3\% of the total fluorescence intensity. The 50-times smoothed data retain the mirror symmetry, but the amplitude was reduced to about 0.2\%. Among these smoothed data, the 5-times smoothed data exhibits the strong holographic oscillation reflecting the symmetry of the single crystal, and it is found to be suitable for the identification of the holographic oscillation in our experimental data. Thus, we applied this numerical procedure to all the \( \chi(\phi, \theta) \) data for 35\(^\circ\) < \( \theta < \) 55\(^\circ\). The full pattern of \( \chi(\phi, \theta) \) is shown in Fig. 2.
where $R$ is the distance between the sample and the detector. As shown in Fig. 3(b), the atomic image of the (001) plane was reconstructed from the hologram in Fig. 3(a). However, the obtained image was not clear and we could not identify atoms around the emitter. The spatial resolution of the reconstructed image is proportional to the size of the hologram. Thus, we took advantage of the four fold symmetry of SrTiO$_3$ (001) and doubled the size of the hologram by combining $\chi(k_x, k_y)$, as shown in Fig. 4(a). This hologram was obtained by combining raw $\chi(\phi, \theta)$ and $\chi(\phi + 90^\circ, \theta)$ data at $\phi = 90^\circ$, followed by smoothing. The atomic image obtained from this hologram is shown in Fig. 4(b). The four nearest Sr atoms at the corner of the grid are visible, but the spatial resolution along the $x$-axis is higher than that along the $y$-axis, because the length of the hologram along the $x$-axis is about twice that along the $y$-axis. Furthermore, we again extended the hologram by combining $\chi(\phi, \theta)$, $\chi(\phi + 90^\circ, \theta)$, $\chi(\phi + 180^\circ, \theta)$ and $\chi(\phi + 270^\circ, \theta)$ in a manner similar to that used to obtain the hologram in Fig. 4(a), and reconstructed the atomic image, as shown in Figs. 5(a) and (b). Four atoms at the corner of the grid in Fig. 5(b) are clearer than those in Fig. 4(b). Thus, the extension of the hologram by making use of the symmetry of the single crystal is useful for obtaining an atomic image with a high spatial resolution.

4. Conclusions

Atomic image of SrTiO$_3$ was successfully obtained from the X-ray fluorescence hologram recorded at the Photon Factory. The holographic oscillation, which could not be seen in the raw data, was recognized after applying the Savitzky-Golay smoothing method. The smoothing technique was useful for judging the quality of the holographic data. Atomic images were reconstructed from three different sizes of the hologram and evaluated as to their spatial resolution. The
spatial resolution of the reconstructed image became higher with larger size of the holograms. The extension of the hologram by making use of the symmetry of the single crystal was useful in obtaining a clear atomic image.

Fig. 5. (a) The hologram of full φ range in k-space and (b) its holographic reconstruction of (001) plane.

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10) Y. Gohshi: personal communication.