

## Local Atomic Image of 0.02 % Zn in GaAs Wafers Using X-ray Holography

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### ABSTRACT

X-ray fluorescence holography (XFH) produces direct three-dimensional atomic images around atoms emitting fluorescent X-rays. However, only the holograms of single crystals, whose atomic configurations are already known by single crystal X-ray studies, have been measured because of the low intensity of the X-ray beam. We used XFH techniques to image the atomic structure around zinc (Zn) atoms doped with gallium arsenide (GaAs) using a synchrotron beam at SPring-8. The Zn K $\alpha$  X-ray fluorescence intensity was measured as a function of azimuthal and polar angles of a detector, to produce a holographic pattern. The local atomic structure around Zn atoms was successfully reconstructed by a Fourier transform of the holograms.

## INTRODUCTION

A fluorescent X-ray photon emitted from a single atom reaches the detector directly without interacting with other atoms in the sample, or by elastic scattering by neighboring atoms. Interference between these two processes produces anisotropy of X-ray fluorescence intensity, which is called X-ray fluorescence holography (XFH). XFH makes it possible to obtain direct three-dimensional atomic images by use of a Fourier Transform method. In 1948, a holographic method was first proposed and performed by Gabor,<sup>1</sup> in order to improve the spatial resolution of an electron microscope image. Szöke<sup>2</sup> pointed out that photon excited atoms within a sample emit highly coherent outgoing electrons or fluorescent X-rays, and he proposed the concept of atomic-resolution holography using an interference effect between the direct waves from the photon excited atom (reference wave) and the waves scattered by neighboring atoms (objective waves) (Fig.1(a)). Electron emission holography<sup>3,4</sup> was thus established for studying surface structure. The internal structure of a solid can not be imaged because of complications produced by the highly anisotropic nature of the electron scattering process and multiple scattering effects. Inner-source X-ray holography has recently become the preferred method of imaging because X-ray scattering produces better images than those produced by electron scattering.<sup>5-8</sup>

In 1996, Tegze and Faigel produced the first XFH image of a strontium titanate ( $\text{SrTiO}_3$ ) crystal.<sup>9</sup> The reconstructed image clearly showed a strontium atom, though the titanium and oxygen atoms were not observed because these atoms have too low an atomic number. The atomic scattering factor is proportional to the atomic number. A disadvantage of XFH is the limited number of characteristic lines from the elements present in the sample. This problem is solved by multiple energy X-ray holography<sup>10-12</sup> (MEXH), which is based on the idea of optical reciprocity of XFH and applying X-ray standing waves principles. MEXH uses a plane monochromatic reference wave from a source far outside the object, as shown in Fig.1 (b). The incident reference wave is scattered by the neighboring atoms and produces spherical object waves, which interfere with the reference wave. This interference pattern varies with as one changes the direction of the incident beam relative to the specimen. The variation of the electrical field intensity at the absorber can be measured by detecting the X-ray fluorescence from the absorber. Thus, MEXH allow holograms to be recorded at an arbitrary energy, which can suppress the twin-image effect.<sup>13,14</sup>

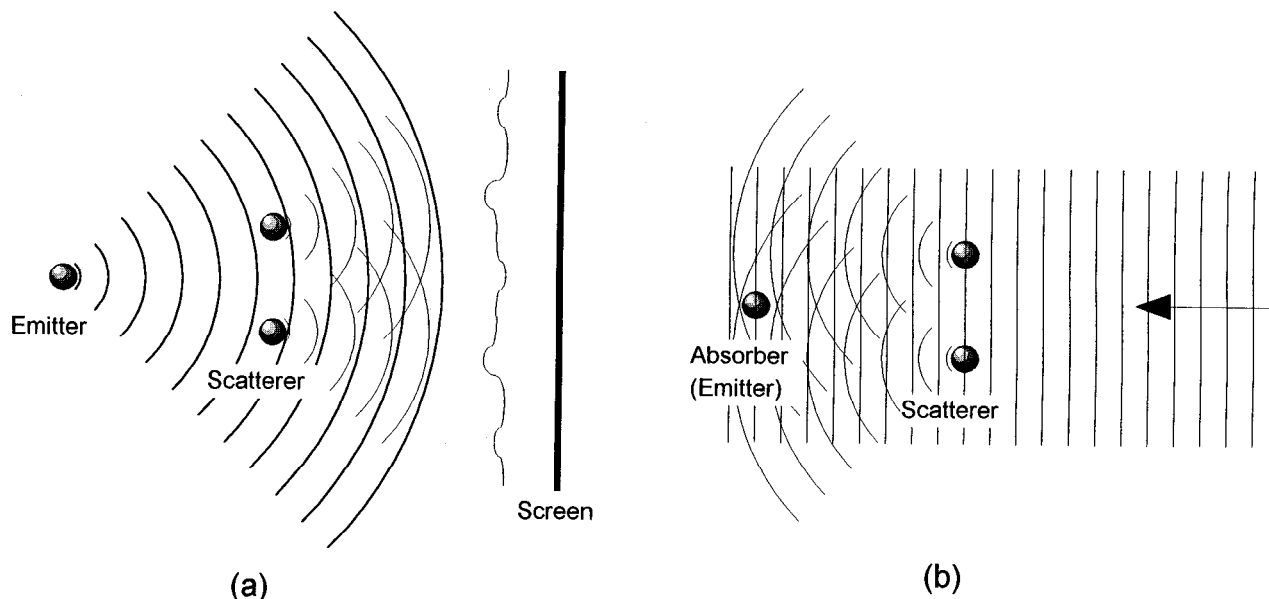


Fig. 1. (a) X-ray fluorescence holography. (b) multiple energy X-ray holography.

Until now, atomic images were obtained only for the major elements of single crystals, whose atomic configurations were already known. We produced an XFH of a  $\text{SrTiO}_3$  single crystal at the Photon Factory<sup>15</sup> and predicted that the hologram of a trace element could be measured using a third-generation synchrotron-radiation facility, SPring-8. We were able to use SPring-8 to measure the hologram of zinc (Zn; 0.02 wt%) doped into a gallium arsenide (GaAs) wafer.<sup>16</sup> In this paper, we show detailed experimental data of the Zn hologram and our mathematical procedure to obtain the reconstructed image.

## EXPERIMENTAL

Data for a hologram was produced on synchrotron beam line BL39XU (Physicochemical Analysis beamline) at SPring-8 (Super Photon ring-8GeV), Japan Synchrotron Radiation Research Institute, Nishi-Harima, Hyogo, Japan. This beamline was equipped with an undulator and a Si (111) double crystal monochromator. The GaAs:Zn wafer

(001) was purchased from Furuuchi Chemical Co. (Tokyo, Japan). The zinc concentration in the wafer was determined to be  $1.0 \times 10^{19}$  atoms  $\text{cm}^{-3}$  (0.02 wt%) by a Hall measurement. The incident X-ray energy was 9.8 keV, which was between the Zn K and Ga K absorption edges, so as to avoid excitation of the Ga and As X-ray fluorescence. The GaAs: Zn wafer emitted characteristic Zn X-rays as well as strongly scattered incident X-rays. Since the limit of the detector count rate was about five thousand counts per second, the counts from scattered X-rays interfered with the detection of the Zn  $K\alpha$  X-ray fluorescence. In order to suppress this scattering, the detector was set parallel to the electric field of the incident X-rays. In MEXH, the fluorescence yield is measured as a function of the incoming beam direction. However, in XFH the X-ray fluorescence intensity from a sample stationary relative to the source is measured while scanning the detector. Therefore, we chose the MEXH method in order to fix the detector position.

Figure 2 shows a schematic illustration of the experimental setup. The sample was mounted on a two-axis ( $\theta - \phi$ ) rotatable stage. A Si PIN photodiode X-ray detector was placed parallel to the incident X-ray electric field, as shown in Fig. 2.

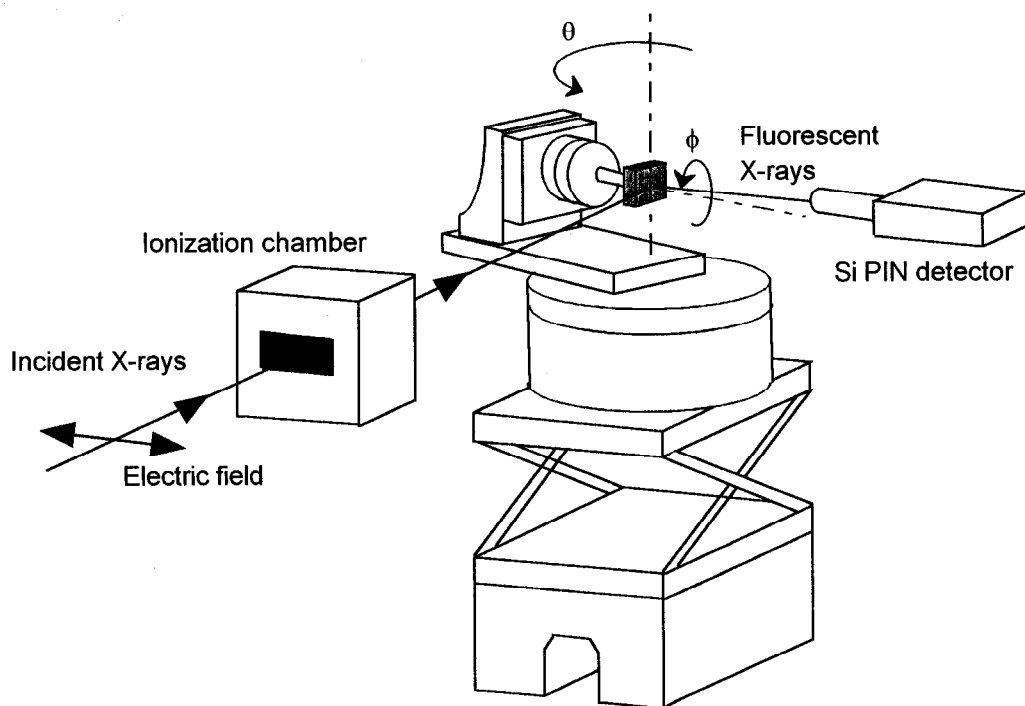


Fig. 2 Schematic illustration of the experimental setup. Zn  $K\alpha$  X-ray fluorescence was measured by changing  $\theta$  and  $\phi$ , where  $\theta$  was the glancing angle and  $\phi$  was the azimuthal rotation angle.

Figure 3 shows the representative X-ray fluorescence spectrum, exhibiting the strong Zn K $\alpha$  X-ray fluorescence. The integrated intensity in the region between 8.0 and 9.0 keV (shaded area in Fig. 3) was measured using a single channel analyzer and an ORTEC 974 counter & timer. 700 data points for fluorescence intensities were collected in a hemisphere above the sample while scanning  $\phi$  and  $\theta$ . The details of experimental condition are shown in Table 1.

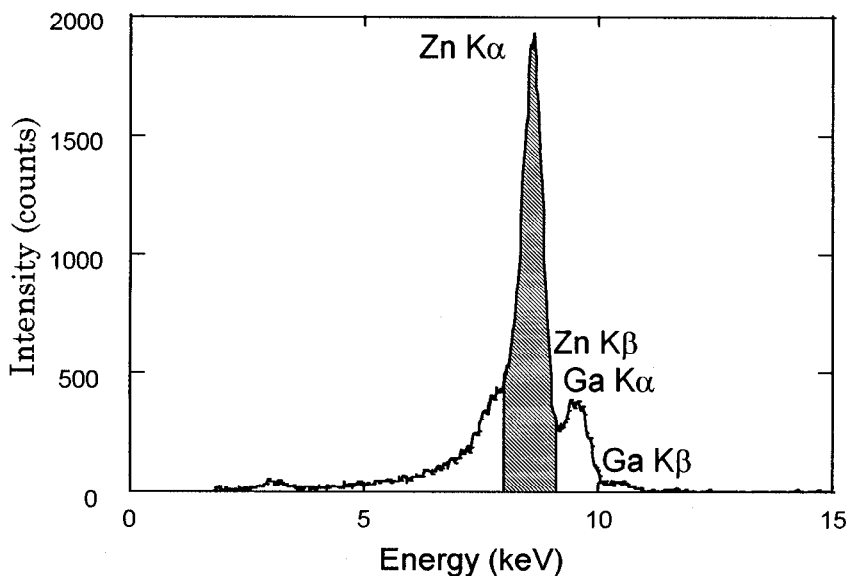


Fig.3 Representative X-ray fluorescence spectrum of Zn in a GaAs wafer.

Sample	GaAs:Zn (001)
Zn concentration	0.02 wt%
Experimental mode	MEXH
Ring current	19 - 17 mA
Incident energy	9.8 keV
X-ray fluorescence	Zn K $\alpha$
$\phi$	$-100^\circ < \phi < 100^\circ$ , $\Delta\phi = 2^\circ$
$\theta$	$30^\circ < \theta < 60^\circ$ , $\Delta\theta = 5^\circ$
Total time	13 hours

Table 1 Experimental conditions

## RESULTS AND DISCUSSION

The procedure to obtain a reconstructed image from the experimental data was done by normalization, smoothing and mapping of the hologram data using the software of *Igor*<sup>®</sup>. This software is used for data visualization, analysis and transformation. The measured Zn 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 a scan. Figure 4 (a) shows the representative

normalized fluorescence intensity at  $\theta = 55^\circ$ ,  $I(\phi, \theta=55^\circ)$ . The peak observed at  $\phi = 162^\circ$  is a Kossel line,<sup>17</sup> which was removed by eliminating  $I(\phi=162^\circ, \theta=55^\circ)$ . The normalized fluorescence intensity  $I(\phi, \theta)$  was transformed into  $\chi(\phi, \theta)$  using following expression,

$$\chi(\phi, \theta) = (I(\phi, \theta) - I_0(\theta)) / I_0(\theta) \quad (1)$$

where  $I_0(\theta)$  was the average intensity over whole  $\phi$  scan range. Figure 4 (b) shows the  $\chi(\phi, \theta=55^\circ)$ . The S/N of the raw data was so poor that anisotropy of the fluorescence intensity could not be seen, because the total count in each pixel ( $\sim 1 \times 10^5$  counts) was not enough to observe the fine structure in the raw data. The solid line in Fig. 4 (b) is the data smoothed twice by a 7 point Savitzky-Golay method.<sup>18</sup> Smoothing clarified the modulation in the anisotropy of the X-ray fluorescence intensity.

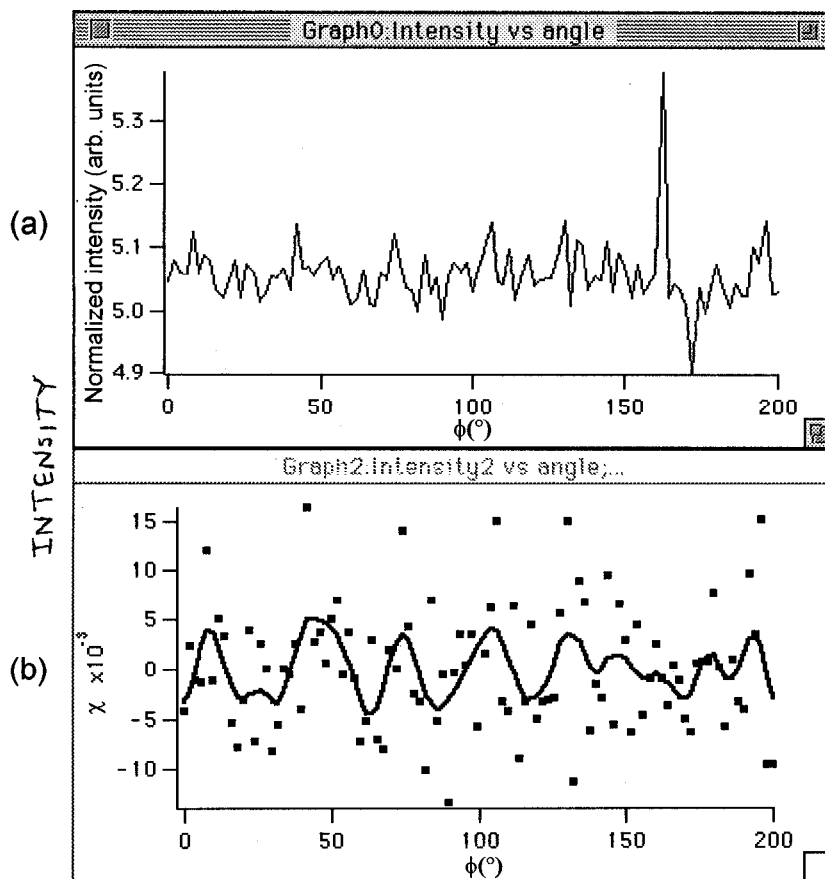


Fig. 4 Angular dependence of the X-ray fluorescence intensity of Zn in a GaAs wafer. (a)  $I(\phi, \theta = 55^\circ)$ ; (b)  $\chi(\phi, \theta = 55^\circ)$ . Dotted and solid lines in (b) are raw and smoothed data, respectively.

Figures 5 (a) is the image of the hologram,  $\chi(\phi, \theta)$  for  $0^\circ \leq \phi \leq 200^\circ$  and  $30^\circ \leq \theta \leq 60^\circ$ . These data were smoothed by the above mentioned procedure.  $\chi(\phi, \theta)$  was converted to  $\chi(k_x, k_y)$  in Fig.5 (b) using following expression,

$$k_x = |k|\sin\theta\cos\phi \quad (2)$$

$$k_y = |k|\sin\theta\sin\phi. \quad (3)$$

where  $|k|$  is the magnitude of Zn  $K\alpha$  wave vector ( $4.97 \text{ \AA}^{-1}$ ).

The real-space atomic image,  $U(x, y)$ , was obtained by the use of a two dimensional Fourier transform of the quantity  $\chi(k_x, k_y)$ :<sup>19</sup>

$$U(x, y) = \frac{1}{2\pi R^2} \iint \chi(k_x, k_y) \exp(ik_x x + ik_y y) dk_x dk_y \quad (4)$$

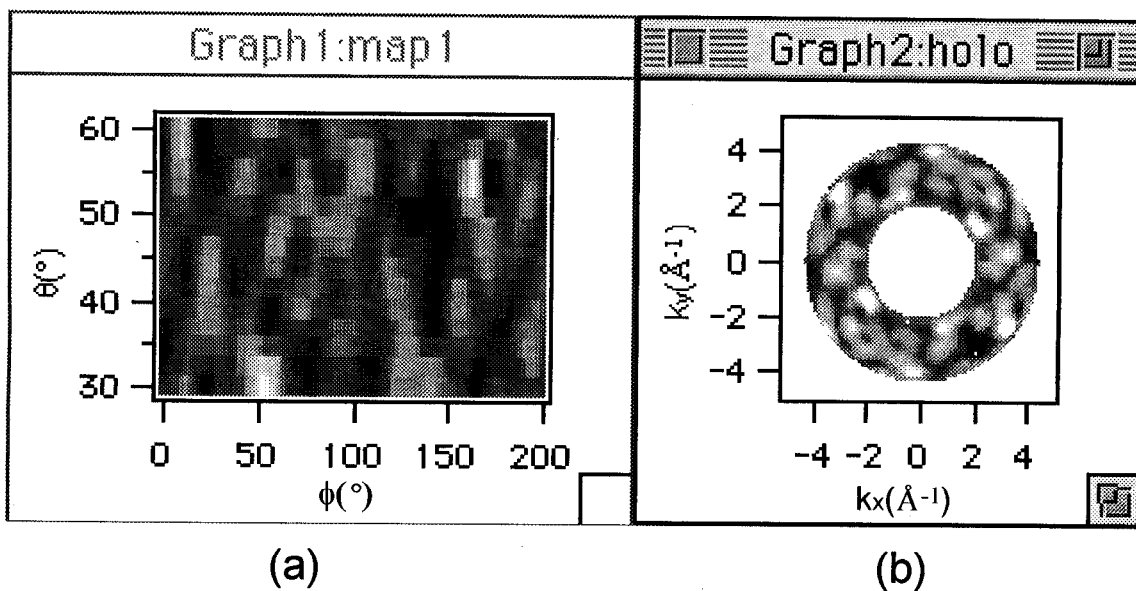


Fig. 5 Experimental MEXH hologram of Zn in GaAs wafer. (a)  $\chi(\phi, \theta)$  and (b)  $\chi(k_x, k_y)$ .

A fourier transform was carried out by use of *NIH Image*<sup>®</sup> software which is a public domain image processing and analysis program for Macintosh, as shown in Fig.6 (a). The atomic image is produced by the environment of Zn atoms on the (001) plane. The reconstruction is affected

strongly by polarization of the incident beam. According to the simulation by Len et al.,<sup>20</sup> a horizontally polarized incident beam enhances the horizontal atomic structure in our experimental configuration.<sup>20</sup> The atomic image in Fig. 6 (a) was improved by the polarization effect. Four atoms were found in the image at a distance of 4.0 Å from the center. This distance is the nearest Ga-Ga or As-As distance, revealing that Zn atoms substituted for Ga or appeared as As host atoms. We also observed four blurred images of atoms at a distance of 2.0 Å from the center Zn atom in Fig. 6 (a). Since Ga and As layers stack alternately along the c-axis; these two layers are separated by 1.41 Å, this image was a superposition of two different Ga or As layers above and below the emitter, because the spatial resolution along z-axis was about 4 Å, which was calculated from the incident X-ray wavelength (1.26 Å) and the size of the hologram.<sup>9</sup> Consequently, Zn atoms occupied the substitutional site, but the possibility of As as a site substitution may be negligible because of the charge neutrality, as shown in Fig. 6 (b).

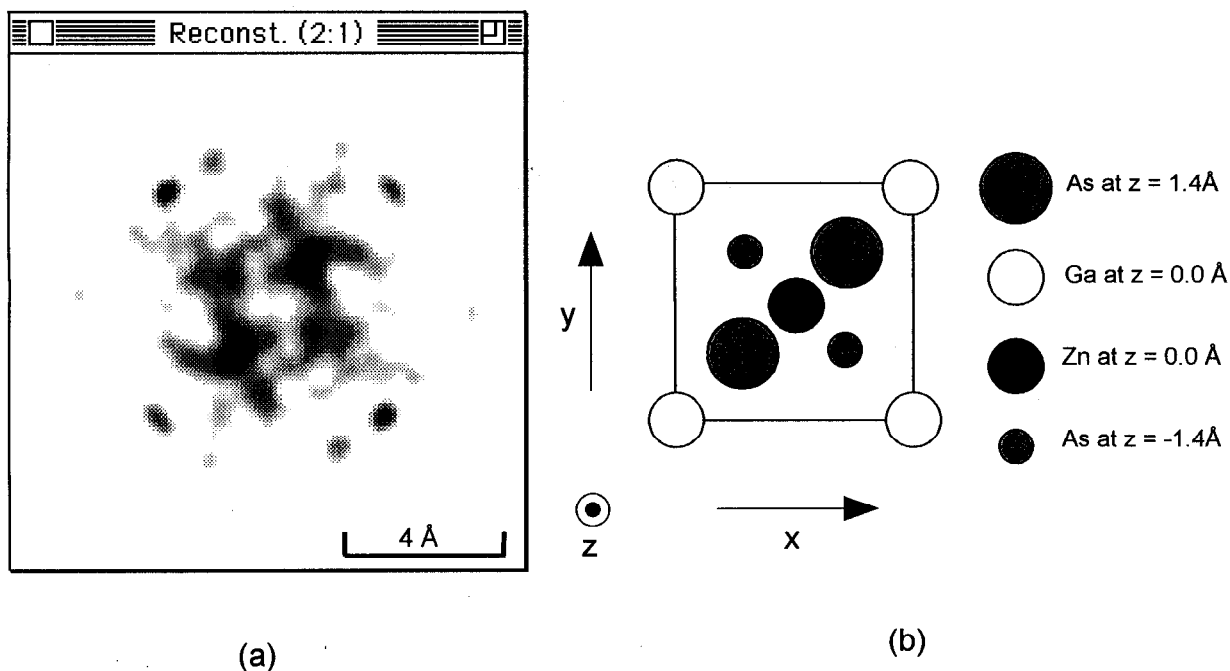


Fig. 6 Reconstructed holographic images around a Zn atom (a) and the atomic configuration of GaAs (b).



## CONCLUSION

The MEXH hologram of 0.02 wt% (200 ppm) Zn in GaAs wafer was measured at SPring-8, and produced local atomic images around Zn atoms. These images revealed that Zn atoms occupied the substitutional site. Our results show that a strong primary X-ray beam from a third-generation synchrotron radiation facility enabled us to measure the hologram of a dopant in a wafer within a reasonable measurement time. The structural analyses of a single crystal using X-ray fluorescence holography was reported in 1996, and this method is still useful for determining the local structure of a trace element in a single crystal, such as dopants in Si wafers, metals atoms in biological macromolecules, and organometallic thin films. In this experiment, the intensity of the incident beam was high enough to produce strong X-ray secondary fluorescence. An X-ray hologram of impurities in the ppm concentration range and of thin films should be possible after the current of the storage of SPring-8 is increased from 20 mA to 100 mA in late 1998.

## ACKNOWLEDGEMENTS

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