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Element-specific hard x-ray diffraction microscopy

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An element-specific coherent x-ray imaging technique using anomalous x-ray scattering in the hard x-ray region was first demonstrated. Coherent x-ray diffraction patterns of a sample composed of 500-nm-thick Ni and Cu layers were measured at incident x-ray energies around the Ni K absorption edge. Non-center-symmetric diffraction patterns due to anomalous scattering phenomenon in the hard x-ray region were observed. Symmetry of the diffraction pattern was quantitatively analyzed by numerically simulating the x-ray wave field behind the sample position using the Rytov approximation. By calculating the difference between the intensities of reconstructed images of different energies, an image of the Ni layers could be derived although it was not enough to identify precisely. This method is widely applicable to nondestructive analysis of nanometer-scale elemental distribution of materials buried within thick and high-Z samples.

The use of the absorption-edge wavelength for elemental identification by CXDM was suggested by Sayre et al. in 1998. The numerical simulation of element-specific CXDM was subsequently carried out before the experiment. Recently, an element-specific technique of CXDM has been realized in an experiment in the soft x-ray region. In this Brief Report, Bi regions in a few-hundred-nanometer-thick Bi-doped Si were identified by CXDM with the resonant x-ray scattering around the Bi M absorption edge. The element-specific CXDM in the hard x-ray region demonstrated in the present Brief Report considers the x-ray wave field behind the sample position using the Rytov approximation in data analysis, allowing us to identify elements in high-Z and thick materials such as metallic samples more than 1 μm in thickness.

To demonstrate element-specific CXDM in the hard x-ray region, a sample composed of Ni and Cu layers was fabricated on a Si3N4 membrane chip. Figure 1 shows a schematic of the sample and a scanning ion microscope (SIM) image. A Ni/Cu film was deposited on a 270-nm-thick Si3N4 membrane by electron-beam evaporation. The thickness of each Ni and Cu layer was about 500 nm. An island of about 1.5 × 1.5 μm² was fabricated on the membrane using a focused ion beam (FIB). The Ni/Cu film in a 100 × 100 μm² area around the island was completely removed. During the FIB milling, the contrast due to the crystal grains of Ni and Cu studies have been performed using synchrotron radiation and a vacuum-ultraviolet free-electron laser and tabletop high-harmonic soft x rays. In particular, CXDM using hard x rays not only has the potential of atomic-resolution observation, but is also a promising tool for the internal structure analysis of hard materials, e.g., metallic materials, thicker than a few hundred nanometers, which cannot presently be observed by TEM.

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Coherent x-ray diffraction measurements were carried out at BL29XUL (Ref. 22) in SPring-8. Incident x rays were monochromated at energies around the Ni K absorption edge using a Si 111 double-crystal monochromator and Pt-coated mirrors. Before measuring the diffraction patterns, the x-ray absorption spectrum of a 10-μm-thick Ni foil around the Ni K absorption edge was measured [Fig. 2(c)]. From the absorption spectrum, the anomalous x-ray scattering factors of Ni around the Ni K absorption edge were derived using the program CHOOCH.23 The incident x-ray energies selected for coherent x-ray diffraction measurements were 8.2125, 8.3225, 8.3360, 8.3405, and 8.4615 keV. The experimental setup for the CXDM measurements is similar to that described in the previous report.17 The Si₃N₄ membrane chip with the logo was placed in vacuum. Incident x rays were irradiated to the sample through a 20-μm-diameter aperture. Forward x-ray diffraction was collected by a charge-coupled device detector with 1300 × 1340 pixels placed 2.809 m downstream of the sample. Diffraction data were collected as a function of the modulus of the scattering vector, \( k = 4\pi \sin \theta / \lambda \), where \( \theta \) is half the scattering angle and \( \lambda \) is the wavelength. The average exposure time of x rays for obtaining each diffraction pattern was 200 s.

Figures 2(a) and 2(b) show the diffraction pattern at 8.2125 keV and its magnified image around the central speckle, respectively. Two speckles at center-symmetric positions are indicated by black circles in Fig. 2(b). To evaluate the symmetry of the speckle intensities at each energy, the ratio of the peak value of the speckles was plotted [Fig. 2(c)]. Above the Ni K absorption edge, the centrosymmetry of the speckle patterns decreases. The present diffraction patterns are therefore thought to include the effect of the anomalous scattering of Ni atoms. This is the first result on the observation of anomalous scattering for coherent x-ray diffraction in the hard x-ray region, although a similar contrast has been reported in an experiment in the soft x-ray region.24 Furthermore, below the Ni K absorption edge, the speckle patterns are also noncentrosymmetric. To quantitatively evaluate the centrosymmetry of the diffraction patterns, the patterns were numerically simulated using the

\[
q = \exp[-ik(\delta + i\beta)],
\]

where \( k \) is the wave number of the incident x rays, \( t \) is the sample thickness, and

\[
\delta = (N\chi^2 r_s (Z + f_z)/2\pi),
\]

\[
\beta = -(N\chi^2 r_s f_z/2\pi),
\]

where \( Z \) is the electron number of an atom, \( f_1 \) and \( f_2 \) are the real and imaginary parts of the anomalous dispersion terms, respectively, \( r_s \) is the classical electron radius, and \( N \) is the number of atoms per unit volume. Here the wave field behind the sample (\( I_0 \)) is normalized using the incident wave field (\( I_0 \)) as \( \chi = I_0 / I \). \( \chi \) and \( \delta \) correspond to the image function reconstructed by the HIO algorithm and the complex transmissivity \( q \) of the sample, respectively. By applying a fast Fourier transform (FFT) to \( \chi \), the far-field diffraction patterns are derived. The experimental diffraction patterns were numerically simulated using the above procedure. Experimental values of the anomalous scattering factors for Ni and theoretical values for Cu were used to calculate \( \delta \) and \( \beta \).
From the result of observing the sample by CLSM, the remaining Ni on the Cu layer was considered in the value of \( \tau \) used in Eq. (1). The intensity ratio of the numerically simulated speckles at similar positions to those selected in Fig. 2(b) was calculated under the condition that the sample is composed of Ni(500 nm)/Cu(500 nm) for the logo and Ni(200 nm)/Cu(500 nm) elsewhere. The result is plotted in Fig. 2(c). The non-symmetric feature of the diffraction pattern is similar to that observed in the experimental result.

The sample images, which correspond to the contrast resulting from the variation of \( \chi \) values, at 8.2125, 8.3360, and 8.3405 keV were reconstructed by the following procedure. (i) A random-complex-number array in real space was generated with a size of 1201 \( \times \) 1201 pixels. An FFT was applied to the real-space array. The magnitudes of the output complex values in the experimentally measured region were replaced with the diffraction data, while the maximum value of the diffraction data was set in every pixel of the central unmmeasured region because of the presence of a direct beam stop. Next, an inverse fast Fourier transform (IFFT) was applied to the complex values. The resultant complex-space pattern shown in Fig. 2(a). Similar roughness can be seen in each plot. Assuming that the thickness at the position in the logo denoted by the arrow in Fig. 2(b) is 1 \( \mu m \), we can estimate that the PV value of roughness around the logo is a few hundred nanometers, which is consistent with the results of both the observation by CLSM and the numerical simulation of the diffraction patterns. In addition, the profile at 8.3360 keV is similar to that at 8.3405 keV, while the intensity profile at 8.2125 keV is about 10% larger than that at the other energies. To explain this intensity difference, values of \( q \) and \( \chi \) were calculated at 8.2125, 8.3360, and 8.3405 keV, which are summarized in Table I. The \( |\chi| \) value at 8.2125 keV is

![Figure 3](image)

**FIG. 3.** (Color) (a) Image reconstructed from the diffraction pattern shown in Fig. 2(a). The pixel size is 17.4 nm. (b) One-dimensional plots of the reconstructions at 8.2125, 8.3360, and 8.3405 keV along the solid red line indicated in (a). Images are normalized by the sum of each reconstructed intensity at the blue regions in (a). Difference images for (c) 8.3360 and 8.3405 keV and (d) 8.2125 and 8.3360 keV.

| Energy (keV) | \( q_r \) | \( q_i \) | \(|\chi|\) |
|-------------|-----|-----|-----|
| 8.2125      | 0.565 | –0.788 | 0.900 |
| 8.3360      | 0.602 | –0.710 | 0.814 |
| 8.3405      | 0.582 | –0.703 | 0.818 |

TABLE I. Calculated values of real \( q_r \) and imaginary \( q_i \) parts of complex transmissivity \( q \) for a Ni(500 nm)/Cu(500 nm) film when incident x-ray energies are 8.2125, 8.3360, and 8.3405 keV. The amplitudes of the reconstruction function (\( \chi = q - 1 \)) were derived from complex transmissivities at each energy.
keV is about 10% larger than those at 8.3360 and 8.3405 keV, which is consistent with the difference in the image profiles in Fig. 3(b). Next, the difference in the images at two different energies was calculated. Figures 3(c) and 3(d) show the difference images for 8.3405 and 8.3360 keV, and 8.2125 and 8.3360 keV, respectively. The logo image can be more clearly seen in Fig. 3(d) than in Fig. 3(c). The bright areas in Fig. 3(d) are thought to result from the Ni element, and also show the experimental error, nonuniqueness of the phase retrieval, and inaccuracy of the image normalization. Clearer contrast will be obtained when the sample is thicker and layers of the embedded metals.

In summary, element-specific CXDM in the hard x-ray region was first demonstrated using a 1-µm-thick metallic sample composed of 500-nm-thick Ni and Cu layers. The coherent x-ray diffraction patterns were measured at incident x-ray energies around the Ni K absorption edge. Non-center-symmetric diffraction patterns due to the x-ray absorption within the sample were observed. These patterns were quantitatively analyzed by the calculation of the complex transmissivities using the Rytov approximation. The sample images were reconstructed by Fienup's HIO algorithm, corresponding to the complex transmissivity subtracted by one. By calculating the difference in the magnitude of two images around the Ni K absorption edge, an image of the Ni layers was derived although it was not obtained with the necessary accuracy due to the sample thickness. The present method can be used to obtain nanometer-scale elemental distributions in thick materials. In particular, this method will be useful for analyzing structures buried within high-Z materials, e.g., impurities and precipitates buried within alloys. We believe that it will provide unique information that cannot be obtained by 3DAP and TEM.

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