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X-ray Reciprocal-Lattice Space Imaging Method for Quick analysis of Buried Crystalline Nanostructure – a Diffraction Method Fixed at an Angular Position

Osami Sakata[1,2], Wataru Yashiro[3,4], Kunihiro Sakamoto[5], and Kazushi Miki[3]
[1]Japan Synchrotron Radiation Research Institute / SPring-8, Kouto 1-1-1, Sayo, Sayo-gun, Hyogo 679-5198, Japan
[2]CREST, JST, Sanbancho Bldg., 5, Sanbancho, Chiyoda-ku, Tokyo 102-0075, Japan
Fax: 81-791-58-0830, e-mail: o-sakata@spring8.or.jp
[3] National Institute of Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
[4] Graduate School of Frontier Science, the University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa-shi, Chiba 277-8561, Japan
[5]Nanoelectronics Research Institute (NeRI), National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Umezono, Tsukuba, Ibaraki 305-6568, Japan

The x-ray reciprocal-lattice space imaging (X-ReSI) method is a single-exposure x-ray diffraction technique which records the reciprocal-lattice pattern of a fixed crystalline nanostructure using a 2D detector. The typical exposure time is a few seconds to a few minutes. We describe the methodology, instrumentation, and expressions used for geometrical analysis in this technique. The technique was applied to study buried Bi nanoline structures. The results of the application reveal that line structures in samples capped with an amorphous Si layer and having no cap layers still remained with a non-detectable amount of the 2 x n atomic structures though Bi nanolines embeded in Si was found to have a 2 x n superstructure having Bi dimer bonds. This underscores the strength of the x-ray reciprocal-lattice space imaging method as a point-and-shoot technique for quick structural analysis.
Key words: crystalline nanostructure, Bi atomic wire, synchrotron diffraction, higher-energy x-rays, " obvious-at-a-glance " diffraction method

1. INTRODUCTION

Electron diffraction is one of the most popular methods for the evaluation of surface structures. However, it cannot be applied to the structural analysis of a sample in air, solution, or buried interfaces due to the electrons ' shallow penetration and escape depths. For such analysis, x-ray diffraction rises as a more suitable method because x-rays are more transparent than electrons.

For precise analysis of such nanostructures using x-ray diffraction, it is essential for the sample angle to be precisely adjusted with respect to the incident x-ray beam to ensure Bragg diffraction from the ultra-fine structure. The orientation of the x-ray detector must also be adjusted to the direction of the diffracted x-rays. To meet these requirements, one must use a multi-axis diffractometer with more than three axes of combinatory rotation (usually four or more axes) equipped with a motorized sample stage for rough adjustment of the sample position and inclination. In order to get crystallographic structural information such as a crystallographic coordination system and a space group, it is necessary to measure not only a single Bragg diffraction point but also at least 100 independent Bragg diffraction points. To achieve this, the sample and the detector are adjusted to appropriate angular positions and the sample is rocked around the position of Bragg diffraction to collect the diffraction intensity information. Conventionally, reciprocal lattice points are taken up one by one. The procedure needs to be repeated for a plurality of reciprocal lattice points. To characterize the conventional method[1], one may say that the x-ray diffraction intensities distributed within a reciprocal lattice space are measured "with a fine-tooth comb". An overall image of the diffraction intensity profile is difficult to get until after the lengthy and time-consuming measurement "with a fine-tooth comb" is completed.

Such a precise x-ray measurement may not provide a straightforward understanding on the change in the overall image of the reciprocal-lattice space caused by a dynamic surface structural change. On the other hand, reflection high-energy electron diffraction (RHEED) provides us with the change in the overall image promptly but is not applicable for structural determination of a nanostructure that exists in air, interface, or solution. A RHEED-like x-ray diffraction demands the use of higher energy x rays than that used in the conventional surface x-ray diffraction. In a typical RHEED measurement, an electron beam with an energy of E_e =15 keV is used. This corresponds to x rays having an energy of E_p=124 keV as defined by E_p=12.4 $/\sqrt{150.4/1000E_e}$. High-energy x-ray scattering and diffraction have been utilized for buried interfaces in particular a liquid surface/interface at the high energy diffraction beamline ID15A at European Synchrotron Radiation Source.[2] We aim to establish our " obvious-at-a-glance" x-ray diffraction method for reciprocal space imaging of solid surfaces and interfaces for up to about 100 keV photons. In this report, the photon energy of 25 keV is used due to limitation by the available energy range at the Surface and Interface Beamline BL13XU in SPring-8[3]. We use this as the starting steps to achieve the 100 KeV target in the future. We outline herein the X-ReSI method for buried solid-solid interfacial analysis. Some parts in this report appeared elsewhere [4] and [5].

2. X-RAY RECIPROCAL-LATTICE SPACE IMAGING METHOD

2.1 Schematic diagram

Figure 1 depicts the concept of X-ReSI. The diffraction conditions or scattering patterns (the Fourier transform) of a one-dimensional (1D) crystal are sheets, which are perpendicular to the 1D sample, located at Bragg positions of the corresponding bulk crystal of the 1D in the reciprocal-lattice space. The fundamental idea is that Bragg conditions for such 1D structures are sheet shapes and are fulfilled much easilier than those for two-dimensional (2D) and three-dimensional (3D) structures. For example, the segmented streaks would simultaneously arise from the intersection; in addition, segmented arcs [6] also appeared using the same experimental configuration. The method combines high-energy and monochromatic synchrotron x rays in grazing incidence to the sample with a 2D detector, which makes it a powerful analysis tool. Its experimental geometry is similar to that of RHEED. The typical exposure time is a few seconds to a few minutes. The reciprocal-lattice space image or a diffraction pattern is recorded using a 2D x-ray detector such as an imaging plate and a pixel array detector. Its overall image indicates a crystal symmetry. One can evaluate nanometer-scale structures such as a crystal dimension and a periodicity of the wires by analysis of the fine structures in the image.

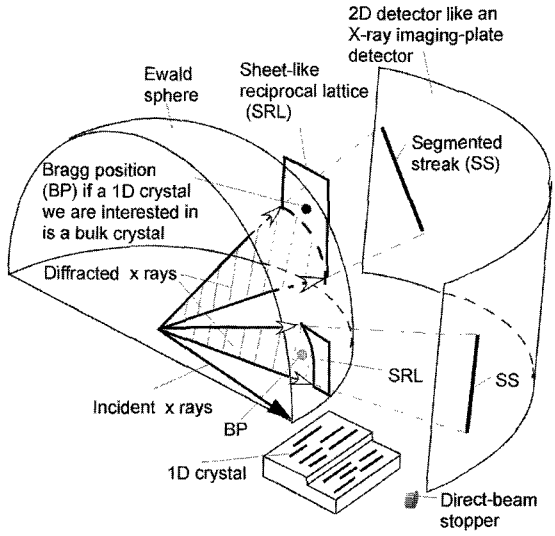

Fig. 1. Schematic diagram for conceptualizing the x-ray reciprocal-lattice space imaging method. Monochromatic and grazing-incidence x rays are incident on a sample fixed an angle. Drawn for the sample of 1D crystal. From Fig. 3 in Ref. [5].

2.2 Expression for diffraction positions on a 2D detector

The experimental setup used is illustrated schematically in Fig. 2. Monochromatic and parallel x rays with wave vector $\boldsymbol{K}_o$ in the horizontal plane are incident on a sample surface which is located at the center of the instrument. We use a ϕ rotary table sitting on a θ inclination table. Let us define two cartesian systems, (X_ϕ, Y_ϕ, Z_ϕ) and $(X_\theta, Y_\theta, Z_\theta)$ attached to the ϕ and θ axes, respectively. These systems will be coincident with a laboratory system (X_L, Y_L, Z_L) for angles ϕ and θ set to zero. Plane $X_L - Y_L$ with Y_L parallel to the incident x-rays is parallel to the horizontal plane.

The sample is rotated through an angle ϕ around Z_ϕ parallel to its surface normal for adjusting an azimuthal angle and independently through an angle θ around X_θ for changing an incident angle. We define unit vectors $\boldsymbol{a}_s^*$ and $\boldsymbol{b}_s^*$ in the reciprocal-lattice space, which make an angle of γ^*, on the sample surface and $\boldsymbol{c}_s^*$ perpendicular to the surface. Here $-\boldsymbol{a}_s^*$ is defined to be parallel to Y_L when angles ϕ and θ are equal to zero. A reciprocal-lattice vector $\boldsymbol{q}_s (\equiv h_s \boldsymbol{a}_s^* + k_s \boldsymbol{b}_s^* + l_s \boldsymbol{c}_s^* = q_x^s \boldsymbol{u}_X^L + q_y^s \boldsymbol{u}_Y^L + q_z^s \boldsymbol{u}_Z^L$; here, $\boldsymbol{u}^L$ is the unit vector in the laboratory system) considered is expressed as follows:

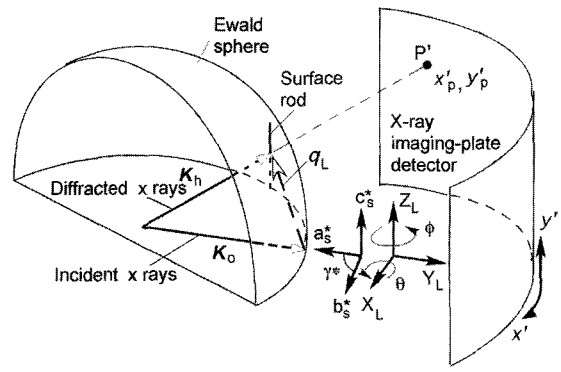

Fig. 2. Schematic representation of the experimental setup for the x-ray reciprocal-lattice space imaging method. Drawn for a 2D crystal. From Fig. 4 in Ref. [5].

$$\boldsymbol{q}_s = \begin{pmatrix} q_x^s \\ q_y^s \\ q_z^s \end{pmatrix} = \begin{pmatrix} b_s^* k_s \sin\gamma^* \\ -a_s^* h_s - b_s^* k_s \cos\gamma^* \\ c_s^* l_s \end{pmatrix}. \quad (1)$$

The reciprocal-lattice vector $\boldsymbol{q}_s$ is transformed to the laboratory system as follows:

$$\boldsymbol{q}_L = R_\theta \, R_\phi \, \boldsymbol{q}_s, \quad (2)$$

$$R_\phi \equiv \begin{pmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$R_\theta \equiv \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix},$$

or in expanded form:

$$\boldsymbol{q}_L = \begin{pmatrix} q_x^L \\ q_y^L \\ q_z^L \end{pmatrix} = \begin{pmatrix} A \\ B\cos\theta - q_z^s \sin\theta \\ B\sin\theta + q_z^s \cos\theta \end{pmatrix}. \quad (3)$$

Here $A = q_x^s \cos\phi - q_y^s \sin\phi$ and $B = q_x^s \sin\phi + q_y^s \cos\phi$. It is noted that A and B are functions of h_s and k_s. A diffracted wave $\boldsymbol{K}_h$ related to the vector $\boldsymbol{q}_L$ is with a wavelength λ therefore

$$\boldsymbol{K}_h = \boldsymbol{K}_o + \boldsymbol{q}_L = (q_x^L, q_y^L + 1/\lambda, q_z^L). \quad (4)$$

If the vector $\boldsymbol{q}_L$ meets a Bragg condition (for example, on a surface rod of a 2D crystal shown in Fig.2), the end of $\boldsymbol{K}_h$ is on the Ewald sphere expressed as follows:

$$(q_x^L)^2 + (q_y^L + 1/\lambda)^2 + (q_z^L)^2 = (1/\lambda)^2$$

which becomes

$$(q_z^s)^2 - \frac{2}{\lambda} q_z^s \sin\theta + \frac{2}{\lambda} B\cos\theta + A^2 + B^2 = 0.$$

Then we have q_z^s and l_s

$$q_z^s(h_s, k_s) = \frac{\sin\theta}{\lambda} + \sqrt{(\frac{\sin\theta}{\lambda})^2 - (\frac{2}{\lambda} B\cos\theta + A^2 + B^2)}, \quad (5)$$

$$l_s(h_s, k_s) = q_z^s / c_s^*. \quad (6)$$

A geometrical consideration that $q_y^L + 1/\lambda : D = q_x^L : x_p = q_z^L : y_p$ leads to an expression for a diffraction position (x_p, y_p) on a plane-type 2D detector

$$x_p(h_s, k_s) = \frac{D\, q_x^L}{q_y^L + 1/\lambda}, y_p(h_s, k_s) = \frac{D\, q_z^L}{q_y^L + 1/\lambda}. \quad (7)$$

In a similar way we obtain (x'_p, y'_p) on a cylindrical-shape detector

$$x'_p(h_s, k_s) = D \arctan \frac{q_x^L}{q_y^L + 1/\lambda},$$

$$y'_p(h_s, k_s) = \frac{D\, q_z^L}{q_y^L + 1/\lambda}. \quad (8)$$

These equations enable us to calculate a diffraction position and l_s using h_s and k_s. Reversely speaking, an observed (x_p, y_p) position gives us the corresponding l_s value.

Comparison between an experimental diffraction pattern and a calculated one allows us to determine angles θ and ϕ. Conversion of the crystal orientations of the sample to an orthogonal coordinate system defined for the measuring system (e.g. laboratory system) is an essential step in structural analysis and measurement of the crystal. This procedure is called determination of the orientation $\boldsymbol{U}$ matrix. This can be achieved by examination of the overall diffraction pattern that is obtained with a single exposure to x rays with the sample and detector fixed in angle and position.[7], [8]

2.3 Instrumentation

In X-ReSI, there is no need for complicated equipment or mechanisms, unlike in conventional diffractometers. For rapid x-ray structural analysis of ultra-fine structures, the angular precision of the rotating mechanism that controls the angle between the sample surface and the incident x rays is 0.0004 °/pulse with a range of ± 5 °. The precision of the height adjusting table associated with the incident angle changing mechanism is 1 μm/pulse with a range of ± 50 mm. The precision of the fine sample adjustment is 0.1 μm/pulse with a range of ± 5 mm. The 2D detector is installed inside a non-rotatable cylinder of which center axis passes through the sample position and which can be installed to the vertical position (see Fig. 3) or horizontal position. The detector can be installed at any angular position within the range of 360 ° about the axis of the cylindrical holder. If a flat 2D detector is used instead, it may also be operated in any desired positions. Another installable feature is a motor that allows sample rotation around the sample normal and a cross table for sample transportation.

3. APPLICATION TO STRUCTURAL OBSERVATION OF BURIED Bi NANOLINE STRUCTURES

We applied the X-ReSI method for quick evaluation to structural analysis of Bi atomic lines buried in the Si epitaxial layer and found that the 2 x n structure parallel to Bi pristine nanowires still remain (shown in Fig.4(C)), which indicated that Bi dimer bonds are parallel to the nanowires.[9] We highlight that the average Bi coverage was smaller than 1/8 monolayers in average from scanning tunneling microscope observation. This underscores the sensitivity of the X-ReSI method. Here, we applied the method two more samples to establish a sophisticated procedure for fabricating a nanoarchitecture: one with an amorphous Si layer and the other without a cap layer. The samples were prepared basically according to the special growth procedure[10]. X-ReSI characterization of the nanoarchitecture shows characteristic streaks blurred with strong diffuse scattering on 00L (shown in circles in Fig. 4(A) and (B)) attributable to the 1D nanoline structure. However, no half-order streaks were observed. In other words, when the Bi nanoline were capped with amorphous-Si or left uncapped, the 1D Bi nanoline structure was preserved but did not have 2 x n superstructures like in the case of the epitaxial Si capping. A summary of the results is tabulated in Table I.

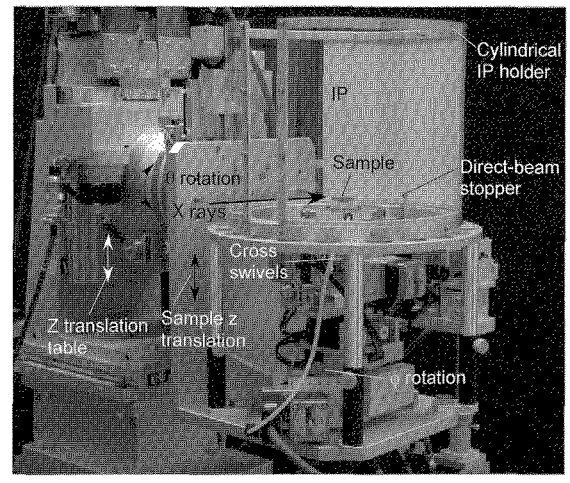

Fig. 3. Compact x-ray camera used for second-to-minute recoding by a reciprocal-lattice space imaging. Shown for the case where a cylindrical two-dimensional detector (colored blue) is mounted in a cylindrical holder installed on a vertical axis. From Fig. 5 in Ref. [5].

Table I. Summary of x-ray reciprocal-lattice space imaging results.

covered by	1D	2 x n
a-Si	remained	not detected
Bi-only	remained	not detected
epi-Si	remained	detected

4. SUMMARY

This report describes our motivation and methodology for establishing the X-ReSI method, and its application to structural observation of buried Bi nanolines. The fundamental idea behind X-ReSI is that the Bragg condition for 1D or 2D crystalline nanostructures are sheets or lines, and are fulfilled much easier than those for a bulk crystalline

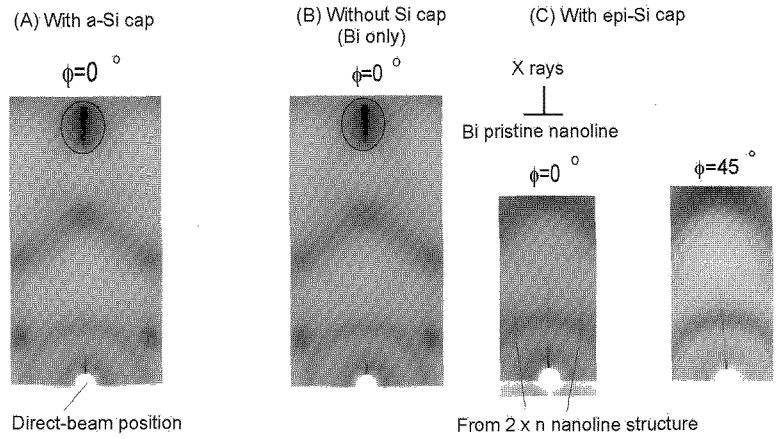

Fig. 4. X-ray reciprocal-lattice space imaging of pristine 1D Bi nanowires on Si (001). Magnified patterns around the direct-beam positions.

material. Accordingly, one does not need to rotate the sample when recording the reciprocal-lattice image using a single x-ray exposure. The typical exposure time is a few seconds to a few minutes. We express the relationship between an index of a reciprocal-lattice vector and its diffraction position recorded on a 2D detector. Application of X-ReSI using the compact camera revealed that line structures in samples capped with the amorphous Si layer and uncapped samples still remained with a non-detectable amount of the 2 x n atomic structures whereas those capped with epitaxial Si showed 2 × n superstructure.

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