Structural characterization of a crystalline film by x-ray diffraction

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After learning at a BL13XU course of this summer school, attendants will realize a conventional and an up-to-date method for characterizing a crystalline film structure using x-ray diffraction. In addition, they will have an experience that the x-ray-diffraction method has an advantage over electron-diffraction one in non-destroyed examination. Furthermore, we hope, they can evaluate film thickness, lattice constants, and crystal domain dimensions of the film from diffraction data sets. In this textbook, we explain the two method using the data that were already published for convenience. Samples used will be an oxide film epitaxially grown on an oxide crystal.

Key words: reflectivity, epitaxial film, c-axis oriented film, reciprocal-lattice space

1 Menu of the BL13XU course

- ★ Introduction of facilities: beamline BL13XU and diffractometer
- ★ Conventional diffraction method
- ★ Obvious-at-a-glance method
- ★ Simulation of x-ray reflectivity curves

2 Main references

With reference to the conventional diffraction:
Sakata *et. al*, Appl. Surf. Sci. **221** (2004) 450.
Sakata *et al.*, J. of Appl. Phys., **96** (2004) 3580.
For the obvious-at-a-glance method:
Sakata *et al.*, Appl. Phys. Lett. **84** (2004) 4239.
Sakata *et al.*, Mat. Res. Soc. Proc., **840** (2005) Q6.4.1

3 Introduction

3.1 BL13XU

Let us first introduce the BL13XU facilities [1] that we used. The light source is the standard SPring-8 in-vacuum undulator (ID) [2] with a 32 mm period and 140 periods. The gap of the ID ranges from 50 mm to 9.6 mm. The fundamental energy range available is correspondingly from 18.9 to 5.5 keV. Figure 1 depicts the beamline layout. The beamline double crystal monochromator with an Si 111 reflection is cooled down with a liquid nitrogen chiller[3]. The two mirrors have two stripes of a rhodium (Rh) and a platinum (Pt) film with a Cr binder. They are for rejecting higher harmonics of incident photons and for focusing an x-ray beam in a horizontal scattering geometry. The monochromator and mirrors are installed in the optics hutch. Experimental hutch 1 is furnished with a multi-axis diffractometer and precision-rotary tables for the structural study of a crystalline interface in air. The former is going to be utilized for the present course.

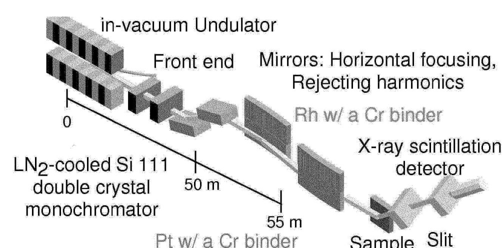

Figure 1: Layout of BL13XU.

3.2 Diffractometer

A six-circle diffractometer (Fig. 2) allows us to measure a diffracted-intensity distribution in the reciprocal lattice space. A scan mode used is called the omega-fixed mode (keeping an omega angle equal to a half of detector angle). We use actually four axes (theta, delta, phi, and chi) of the diffractometer. A sample will be mounted on an

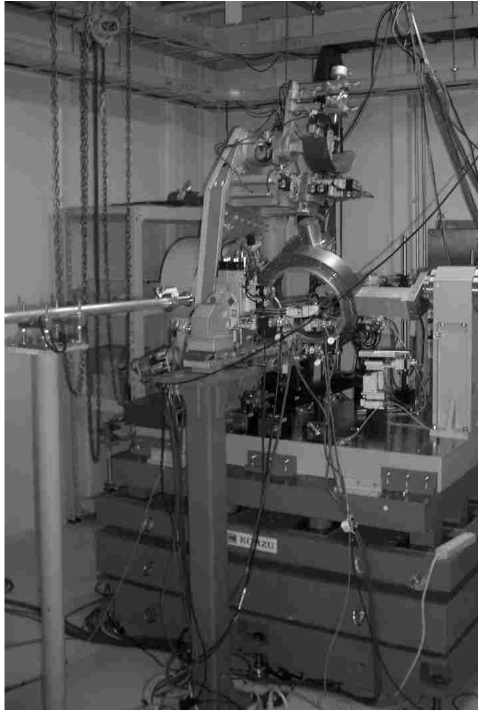

Figure 2: Six-circle diffractometer we are going to use.

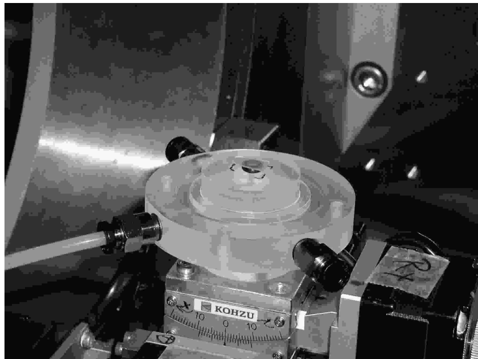

Figure 3: Sample holder monted on a goniometer head.

acrylate holder and pumped through an o-ring for keeping its position . It is the best way to maintain a sample clean and to exchange it (Fig. 3) as far as I know.

4 Conventional diffraction method

Let me explain what the conventional diffraction method is and what kind of structural information we can obtain. We usually use some scans of reflectivity, rocking, azimuth, and H (K, L, or HK) scans. Reflectivity and powder-like are scanned along Q_z in Fig. 4. Rocking scan means that the sample at a reciprocal point is only rocked around the origin of the reciprocal lattice space. By an azimuth scan, the sample is rotated around its

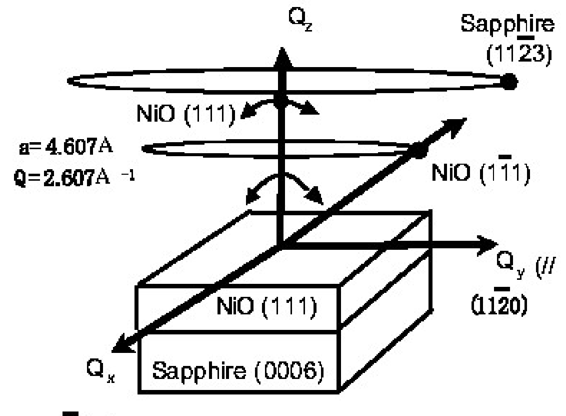

Figure 4: Scans measured in the reciprocal lattice space.

surface normal. H scan is to measure a diffracted / scattering intensity along Q_x. Traverse scan looks like but different from a rocking scan. A q-distance from the origin is the same for any measurements point in traverse scan (an x-ray detector also rotates). We have examples of a reflectivity, azimuth and L scan here.

4.1 Examples

4.1.1 Reflectivity scan–> thickness

Figure 5 shows a reflectivity (R) curve. We evaluated the thickness $\Delta T = 68.7nm$ of the NiO film, being inversely proportional to the periodicity Δq of the oscillation of the curve using eq. 1. It is noted that the intensity is plotted as a function of the reciprocal space unit, being equal to $\frac{2\pi}{d-spacing}$. Then $\Delta T = \frac{2\pi}{\Delta Q_z}$(eq. 1)
R will decrease in proportional to Q_z^{-4} for material with an ideally flat surface but actually decay more rapidly because of surface and interface roughness. We will thus determine the roughness by comparison with a calculated R curve based on a model structure.

4.1.2 Azimuth scan–> epitaxy

Fgure 6 shows an epitaxial relationship between the film and the sapphire substrate. The epitaxial relationship of the NiO films is
NiO(111) // Sapphire (0001), NiO[1 $\bar{1}$ 0] // sapphire [1 1 $\bar{2}$ 0] and was already shown in Fig. 4.

It is noted that the azimuth scans (Fig. 6 show a six-fold symmetry, which was different than we expected from the substrate-crystallographic symmetry. Thus we conclude that the NiO film has anti-domains. NiO on any adjacent terrace has

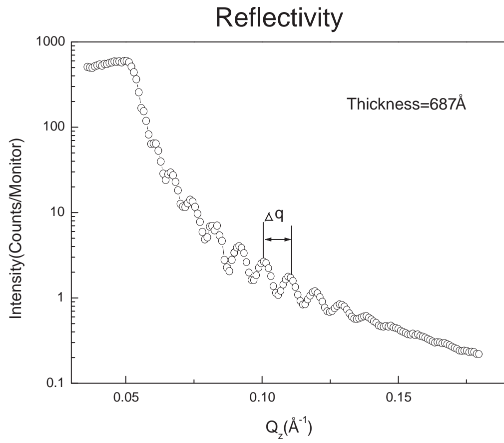

Figure 5: X-ray reflectivity obtained from NiO epitaxially grown on a sapphire substrate.

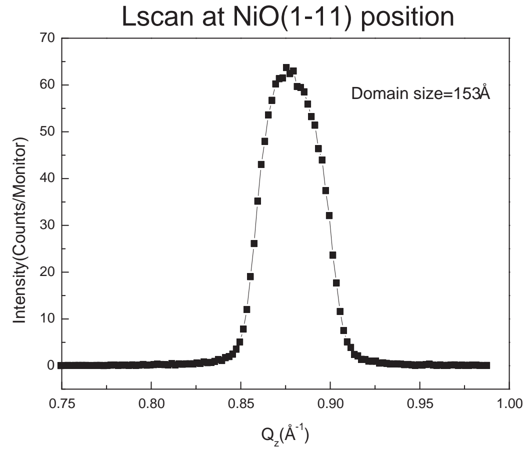

Figure 7: L scan.

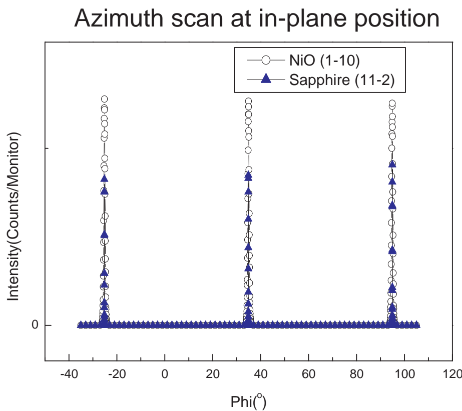

Figure 6: Rocking scan around the NiO 1 $\bar{1}$ 1) and sapphire 1 1 $\bar{2}$ 3 reflection.

an anti-domain structure since the step height of the sapphire substrate is almost half of the [111] length of the NiO unit cell.

4.1.3 L scan–> crystal domain dimension

Figure 7 show results of an L scans around the NiO 1 $\bar{1}$ 1 position. The L direction was almost perpendicular to the sample surface. A domain size D_L (using eq. 1) is 15.3 nm along the L direction, namely out-of-plane direction. We can also make H and/or K scan to obtain an in-plane domain size.

4.1.4 Bragg (HKL) position–> lattice parameter

We can define a reciprocal-lattice space based on lattice parameters of a substrate crystal. This is because the parameters must be known. When indexing a Bragg position (like HKL) for a film, we can estimate the lattice parameters of the film from the HKL position in principle.

4.2 What to do before such scans ?

4.2.1 Alignment of the BL13XU x-ray optics:BL monochromator and BL mirror etc.

You should choose an ID gap and a monochromator angle according to an x-ray photon energy you want to use. You need to fine-tune an angle $\Delta\theta_1$ of the monochromator by monitoring a direct beam intensity with a Si pinphoto diode and adjust an angular and spatial position of BL mirrors (Find a table at BL13XU). The mirrors function

to remove x-ray harmonics and to focus an incident beam. You need to define an incident slit if you like and scan the slit to choose a beam position you like as well.

4.2.2 Centering a diffractometer position and its angular axes

Important is that we must locate a center of all the axes of the diffractometer at that of an incident x-ray beam. You will mount a special "Jigu" which has two piholes and should be put at the chi circle. A diameter of the pinholes can be changed from 3 mm to 0.1 mm. After this alignment, we have axes of theta and mu defined as 0 and the diffractometer properly positioned. In addition, you will further rotate a detector arm around the horizontal for determining δ=0.

4.2.3 Sample alignment from its physical shape

After going to all angles =0 except χ =90 $^\circ$ (making a sample parallel to the horizontal) and mounting a sample, you will move it up/down until you have got a half intensity of the direct beam. You could adjust sample's tilt angles (I mean, two swivels) using a specular intensity. For example, you rotate axis δ to 0.4 degree and axis θ to 0.2 degree. Then you should to record a intensity with rotating one swivel. You will find the maximum intensity at a swivel angle and then go to the angle. You rotate the sample around axis ϕ and do for the other swivel in a same manner.

4.2.4 $\boldsymbol{UB}$ matrix

$\boldsymbol{UB}$ matrix is a product of a $\boldsymbol{U}$ matrix and a $\boldsymbol{B}$ matrix. The $\boldsymbol{B}$ matrix is to convert a $\boldsymbol{h}$ (diffraction) vector expressed using a non-orthogonal system to a new $\boldsymbol{h}$' vector described using the orthogonal system. The $\boldsymbol{U}$ matrix is called an orientation matrix, transforming the $\boldsymbol{h}$' to a vector described using a laboratory system. To make the UB matrix, a pair of angular positions for independent reflections and wavelength are needed. We, first, make a pseudo or fake $\boldsymbol{UB}$ matrix using imaginary angles and reflections to find such real reflections.

Let us assume that a sample crystal considered has a cubic system with a (001) surface. Imaginary information is, for example, as follows: θ_1, δ_1, $\chi_1(=0)$, $\phi_1(=0)$ for the imaginary 1 0 0 diffraction and $\theta_1 + 90°$, δ_1, $\chi_1(=0)$, $\phi_1(=0)$ for the imaginary 0 $\bar{1}$ 0 diffraction. Once having the fake $\boldsymbol{UB}$ matrix, we can calculate angular positions for an arbitrary reflection. Then we move on two real reflections and tune angular positions of θ, δ, χ, and ϕ. The final angular positions for the real reflections provide us with an authentic $\boldsymbol{UB}$ matrix. Accordingly, we can measure diffracted intensities in the reciprocal-lattice space.

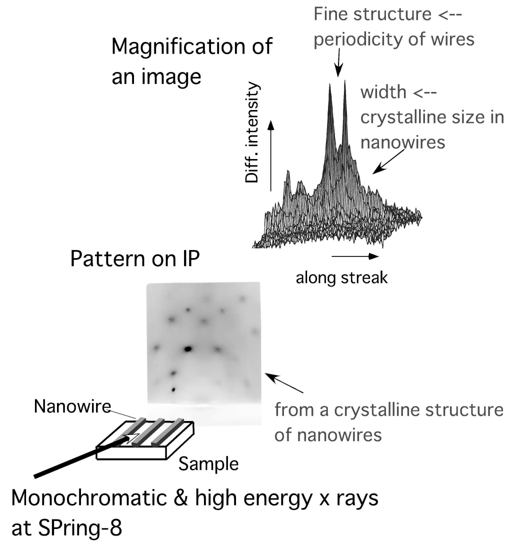

Figure 8: Image of the obvious-at-a-glance method

5 The obvious-at-a-glance method

X-ray diffraction is a promising nondestructive method for determining atomic-scale structures. X-ray scattering/diffraction techniques have revealed surface / interface structures. In particular, the conventional x-ray surface-diffraction approach through maps x-ray intensities diffracted /scattered around Bragg conditions in a reciprocal-lattice space, resulting in determination of a sub-angstrom-scale structure. While being suitable for refining such a structure model, it takes much time. It would be informative quickly to screen samples before this approach. As you read, the conventional diffraction method needs rotation of a sample and a detector. To establish a rapid structural characterization method, Sakata has developed an "obvious-at-a-glance " analysis or " min-exposure " one using reciprocal-lattice space imaging. Rod-shape or Sheet-shape diffraction emanating from a 2D or 1D crystal will be observed from a fixed sample using a 2D detector. Fig. 8 shows the setup and image of the method, which might be classified into a sort of monochromatic Laue method in a reflection geometry. The method needs high energy and monochromatic x rays.

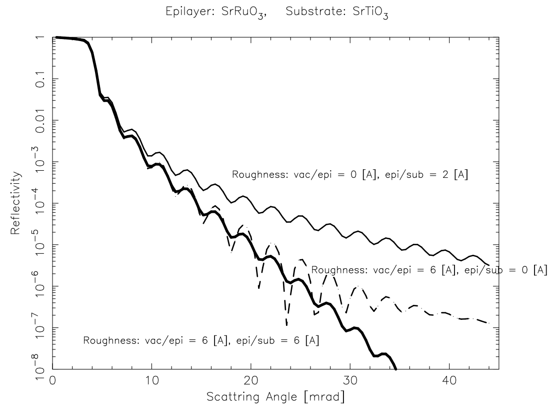

Figure 9: Calculated reflectivities vs. scattering angle for a film on a substrate.

6 Simulation

Let us simulate reflectivity curves. You need to calculate refractive indices of a film and substrate in advance.

Could you bring your pc please If you like.

References

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