X-ray thin-film measurement techniques

II. Out-of-plane diffraction measurements

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1. Introduction

A thin-film sample is two-dimensionally formed on the surface of a substrate, and the film thickness is usually very small, about 1 μm or less. It can be difficult to use a conventional powder diffractometer to acquire high-quality diffraction data from a thin film because thin-film diffraction peaks are usually weak, and the background intensities caused by diffraction and scattering from the substrate are very high. It is known that preferred orientation or anisotropic lattice distortion can have a strong effect on physical properties of thin films, so that it is indispensable to reveal structural or textural properties of thin films using X-ray diffraction techniques with proper X-ray optics.

A description of X-ray optics for various diffraction methods have been given in Section 2.3 of the first article in this series[1]. Generally speaking, X-ray diffraction techniques can be divided into two groups in terms of sample geometry; "out-of-plane" diffraction or "in-plane" diffraction. Out-of-plane diffraction is the most commonly used experimental technique for studying powder, bulk and thin-film materials. This article describes the out-of-plane diffraction measurement techniques and their applications to the determinations of crystal structures of thin films[2],[3].

2. Out-of-plane diffraction

2.1. Out-of-plane diffraction techniques for thin-film analysis

Out-of-plane diffraction can be obtained by either symmetrical or asymmetrical reflections from lattice planes in a sample. A symmetrical-reflection measurement is used to collect diffracted X-rays from crystal lattice planes that are parallel to the sample surface. It means that a symmetrical-reflection measurement is used to obtain crystallographic information along the perpendicular direction to the sample surface. An asymmetrical-reflection measurement is used to obtain diffraction signals from lattice planes that are inclined to the sample surface. Figure 1 shows schematic diagrams of the geometries for the symmetrical- and asymmetrical-reflection measurements.

In symmetrical reflection (Fig. 1 left), both angles of the incident and the diffracted X-rays against the sample surface plane are equal and usually about several to tens of degree. As a result, the incident X-ray beam penetrates deeply into a sample to a maximum of tens of μm. Since the thickness of a thin film is commonly about 1 μm or less, thin-film diffraction intensities obtained by the symmetrical-reflection measurement are generally very weak and often buried under the tail of the strong substrate diffraction peak. The well-known $2\theta/\theta$ scanning technique is used widely to gain diffraction intensities in a symmetrical-reflection measurement.

On the other hand, the asymmetrical-reflection measurement (Fig. 1 right) can be used to measure diffraction peaks from a thin film. This measurement is performed under a specific diffraction geometry in which the incident X-ray beam is kept at a small angle (α; usually about several degrees or less, see Fig. 1 right) with respect to the film surface, and the detector on 2θ axis is scanned to record diffraction intensities from a thin film. This method is also called as a "Thin film method". The X-ray penetration depth inside a thin film can be controlled to several μm or less (also refer to the Section 2.2). Therefore, the asymmetrical-reflection measurement can used to obtain high diffraction intensities from thin film samples, and simultaneously can suppress signals from substrates.

2.2. X-ray penetration depth

X-ray penetration depth in a thin film is a function of the incident angle. The smaller the incident angle, the smaller the penetration depth. It is possible to analyze the change of crystalline phases from the surface to the interior of a thin film by using various incident angles.

How deep X-ray is penetrated into the sample? The intensity of the incident X-ray for any materials does not become zero at any one depth but decreases exponentially with distance x below the surface by X-ray absorption. The function about the absorption behavior

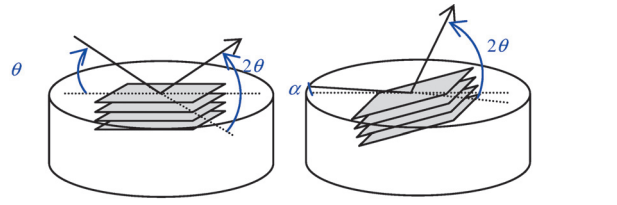

Fig. 1. Geometries for out-of-plane diffraction.

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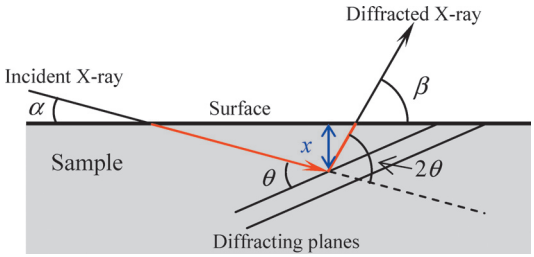

Fig. 2. X-ray diffraction geometry for the asymmetrical-reflection.

is derived from Lambert–Beer law as shown in Eq. (1).

$$I=I_0\cdot e^{-\mu x} \tag{1}$$

I: Observed X-ray intensity
I_0: Incident X-ray intensity
μ: Linear absorption coefficient
x: Sample thickness

In case of X-ray diffraction geometry for the asymmetrical reflection as shown in Fig. 2, X-ray path length l (red line) through the sample for a depth x is expressed as Eq. (2) from the incident angle α, the exit angle β and Bragg angle θ.

$$\begin{aligned} l &= x\left(\frac{1}{\sin\alpha}+\frac{1}{\sin\beta}\right) \\ &= x\left(\frac{1}{\sin\alpha}+\frac{1}{\sin(2\theta-\alpha)}\right) \end{aligned} \tag{2}$$

If the total diffracted intensity by a sample of infinite thickness is 1, the fraction of total diffracted intensity G_x by the depth x for Fig. 2 geometry is expressed as Eq. (3) from Eq. (1) and Eq. (2).

$$G_x = 1-e^{-\mu x\left(\frac{1}{\sin\alpha}+\frac{1}{\sin(2\theta-\alpha)}\right)} \tag{3}$$

$$x=\frac{-\ln(1-G_x)}{\mu\left(\frac{1}{\sin\alpha}+\frac{1}{\sin(2\theta-\alpha)}\right)} \tag{4}$$

Now, if we decide that the depth which the fraction of total diffracted intensity G_x become 0.99 is X-ray penetration depth t, t shows in the following equation.

$$t=\frac{4.61}{\mu\left(\frac{1}{\sin\alpha}+\frac{1}{\sin(2\theta-\alpha)}\right)} \tag{5}$$

In the case of the symmetrical reflection, $\alpha=\beta=\theta$, and Eq. (5) becomes as Eq. (6)[4].

$$t=\frac{4.61}{2\mu}\cdot\sin\theta \tag{6}$$

The calculation results of the symmetrical reflection and asymmetrical reflection for Si(111) and Cu-Kα X-rays from Eq. (5) and Eq. (6) are shown as follows:

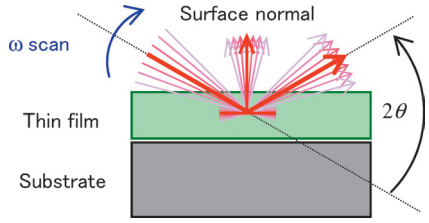

Fig. 3. Rocking curve measurement.

Symmetrical reflection: 38.4 μm,
Asymmetrical reflection with $\alpha=0.5°$: 2.7 μm.

The lattice planes observed in an asymmetrical-reflection measurement are increasingly tilted with increasing the diffraction angle, 2θ. This is a significantly different from those in a symmetrical-reflection measurement, in which lattice planes observed remain parallel to the sample surface throughout the entire measurement. Therefore, the asymmetrical-reflection measurement should be applied for studying a polycrystalline thin film with random or weak preferred orientation. On the other hand, an asymmetrical-reflection measurement is not suitable for the analysis of a strongly preferred-oriented or an epitaxial thin film, because the film has a unique crystal-orientation direction (or axis) perpendicular to the films surface. When the symmetrical-reflection measurement is used for measuring diffraction peaks from a strongly oriented or an epitaxial film, the sample orientation should be checked and aligned to the goniometer system prior to the measurements (see the next section).

2.3. Rocking-curve measurement for studying preferred-orientation in a thin film

It is well known that the preferred orientation direction (or axis) and the degree of orientation are two important factors that can strongly affect the physical properties of a thin film. The orientation axis (or the texture) can be determined by a symmetrical reflection measurement, and the degree (or distribution) of preferred orientation can be obtained by a rocking-curve measurement as shown in Fig. 3. This method is performed by rocking the thin-film sample while the detector is kept a fixed 2θ angle to record diffraction intensities from the preferentially-oriented lattice planes. The degree (or distribution) of preferred orientation is estimated from the full width at half maximum (FWHM) of the rocking curve profile.

An example of a rocking curve measurement is given in Section 4.2.

3. X-ray optics for out-of-plane diffraction

Two types of X-ray optics can be used for out-of-plane diffraction measurements, i.e. focusing optics and parallel-beam optics.

3.1. Focusing optics

The Bragg–Brentano focusing optics has been widely used in X-ray powder diffractometry. The focusing

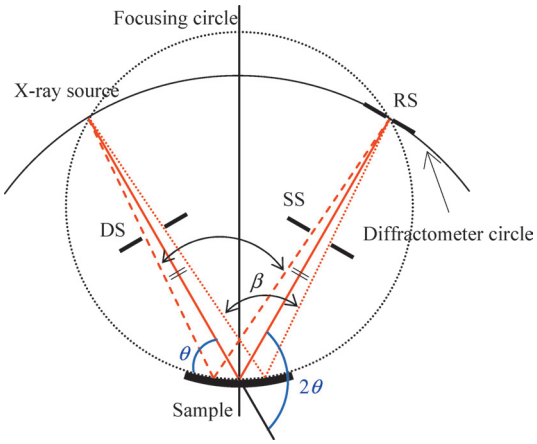

Fig. 4. Focusing optics.

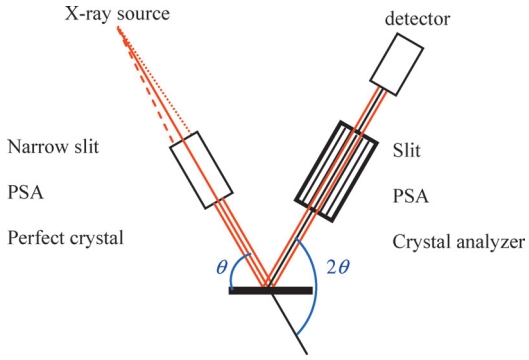

Fig. 5. Parallel-beam optics.

optics is used for the data collection of symmetrical reflections from crystal planes that are parallel to the sample surface. This optics makes full use of a divergent incident X-ray beam to obtain high diffraction intensities and has high resolution.

Figure 4 shows the focusing optics used in a conventional powder diffractometer. The center of the sample is positioned at the center of the diffractometer, and both the X-ray source and the receiving slit (RS) are located at the circumference of the diffractometer circle. For focusing optics, the divergent incident X-rays, after being diffracted by the sample, are focused at the RS position. The locations of the X-ray source, the sample and the RS form a focusing circle. The radius of the focusing circle changes depending on the diffracted angle 2θ and namely the d-spacing of the diffraction planes.

As shown in Fig. 4, there are also two other slits, i.e. divergence slit (DS) and, scattering slit (SS). The DS is installed between the X-ray source and the sample, and the SS is placed between the sample and the RS. The DS controls the divergence of the incident X-ray beam and also limits the X-ray beam to fall within the length of the sample. SS is used to cut off other parasitic scattered (non-diffracted) X-rays from entering the RS and hence, being detected by the detector. In a conventional $2\theta/\theta$ scan, both the detector and the RS are scanned at twice the speed of the sample. The θ and the 2θ angles keep a relation of $\theta : 2\theta = 1 : 2$ at all angles.

Ideally, the focusing optics can provide high diffraction intensities and has high resolution. However, geometrical and physical aberrations caused by axial divergence, flat specimen, specimen transparency, specimen surface displacement, etc. can lead to peak displacements, lower peak intensities, broader peak widths and/or asymmetrical peak profiles[4]. Therefore, special cares to the optics and sample configuration are indispensable, when this optics is applied to thin film samples.

3.2. Parallel-beam optics

In parallel-beam optics shown in Fig. 5, the incident divergent X-ray beam is converted into a parallel beam by employing optical elements, such as, a set of very narrow slits, a parallel-slit collimator (PSC), or a crystal collimator before the X-ray beam impinges onto the sample surface. A narrow slit, a parallel-slit analyzer (PSA), or a crystal analyzer is also used in the diffracted beam to allow only a parallel diffracted X-ray beam entering the detector. Parallel-beam optics has no aberrations similar to those in focusing optics. It is possible to obtain accurate diffraction angles using a parallel incident X-ray beam. A parallel beam has also been used in an asymmetrical-reflection measurement of thin-film structure and residual stress in a sample.

A parallel beam obtained by a narrow slit or by crystal collimation from a divergent X-ray source has weak intensity for analyzing a polycrystalline thin film or a powder sample, except a strongly preferred-oriented thin film or an epitaxial thin film.

In the last several years, however, the advances in thin-film deposition techniques have made possible the fabrication parabolic graded multilayer mirrors. A graded multilayer mirror is made of alternated heavy and light element layers to effectively convert a divergent incident X-ray beam into a high-intensity and parallel beam[5]. The X-ray optics, which makes full use of the characteristics of a parabolic graded multilayer mirror, is shown in Fig. 6.

A graded multilayer mirror can produce a parallel X-ray beam with divergence of 0.04° or less. The mirror also monochromatizes the incident X-rays. For Cu X-rays, the Cu-Kβ intensity is significantly suppressed to only about 0.5% of that of the Cu-Kα intensity. An incident slit before the sample can be used to limit the length of the incident beam to 1 mm or less. A long PSA made of a set of closely spaced and parallel thin-metal plates, is placed between the sample and the detector to obtain high intensities and high angular resolution[6]. Two sets of Soller slits, one on the incident beam side and the other on the diffracted beam side can also be used to limit possible axial divergence (in the direction perpendicular to the figure in Fig. 6) of both incident and diffracted X-ray beams.

3.3. Selection of X-ray optics

As described above, focusing optics is mainly used

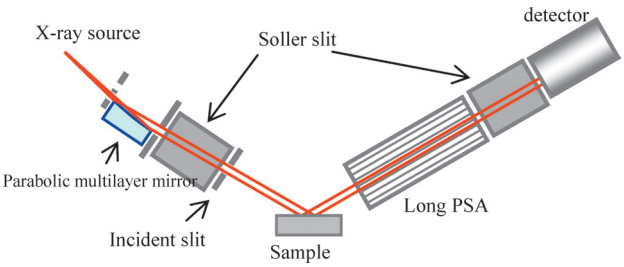

Fig. 6. Parallel-beam optics with a parabolic multilayer mirror.

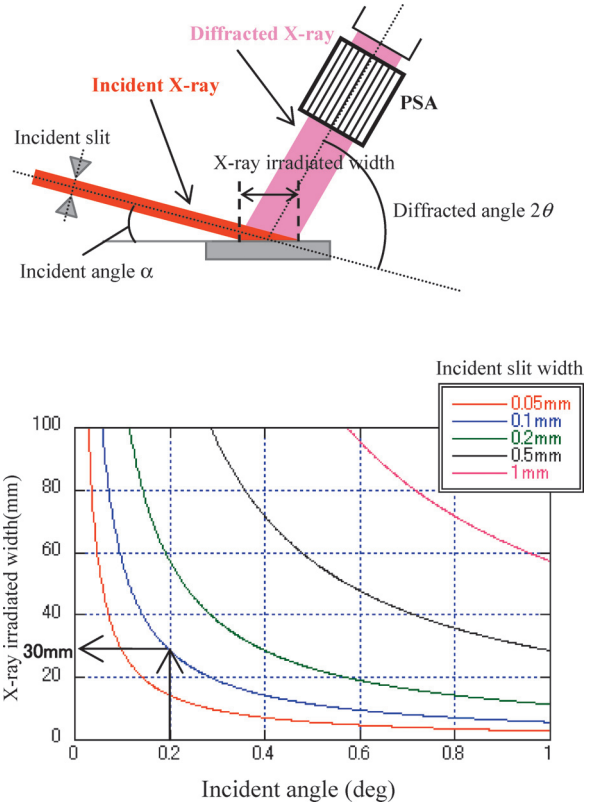

Fig. 7. A schematic view of optical elements employed in the asymmetrical-reflection measurement (upper) and relationship between the incident angle and X-ray irradiated width (lower).

in the symmetrical reflection measurement for powder samples. It is also possible to use focusing optics for studying thin films. If a thin film is with strong preferred orientation, only diffracted peaks from a certain (*hkl*) set of reflections can be detected. When a sample is very thin, diffraction peaks will be very weak and often buried under the strong diffraction peaks from a substrate. This is also true for the symmetrical-reflection measurement using parallel-beam optics.

As described in Section 2.2, the asymmetrical-reflection measurement is suitable for the characterization of thin films. Since the incident angle of the asymmetrical-reflection measurement is fixed at a very small angle, the incident X-ray beam can easily spill over the surface of a sample. An incident slit is therefore often used to limit the incident X-ray beam to

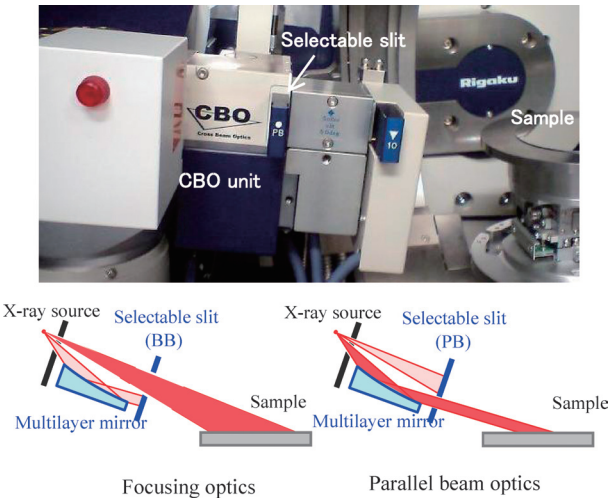

Fig. 8. Schematic diagram of a CBO system.

fall within the sample surface. A plot of the X-ray irradiated length (or width) vs. the incident angle for various incident slit widths is given in Fig. 7. For example, the irradiated length is 30 mm for an incident angle of 0.2° and an incident slit width of 0.1 mm. If the X-ray irradiated length is longer than the width of the sample, the spilled-over X-rays will irradiate the sample holder and probably cause undesirable scattering and sometimes diffraction from the holder, resulting in high background noises. It is important to select an incident slit with a proper width to eliminate unwanted X-ray signals. Since the length of the diffracted beam is usually long, a PSA with a wide receiving window is needed to get both high intensities and high resolution (see the upper figure in Fig. 7).

As shown above, parallel-beam optics is not only used in the symmetrical-reflection measurement, but also in the asymmetrical-reflection measurement for thin-film and rocking curve measurements including “thin-film method”. It should also be noted that the use of a multilayer mirror together with a channel-cut crystal can improve monochromatization and collimation of the incident beam. This combination of optical elements can be used in a high-resolution rocking curve measurement for the evaluation of lattice constants of an epitaxial film and its substrate, as well as a measurement of strain/relax of a thin film on the substrate, etc.

Figure 8 shows a latest general-purpose X-ray diffractometer equipped with an advanced Cross Beam Optics (CBO^{TM}) unit in the incident X-ray beam. With a CBO, divergent-beam and parallel-beam optics, which have different optical paths, can be switched by simply pushing the optical selectable slit[7].

4. Examples

4.1. A polycrystalline silicon thin film on a glass substrate

The X-ray diffraction patterns of a polycrystalline silicon film (t=10 nm) deposited on a glass substrate obtained by using symmetrical- and asymmetrical-

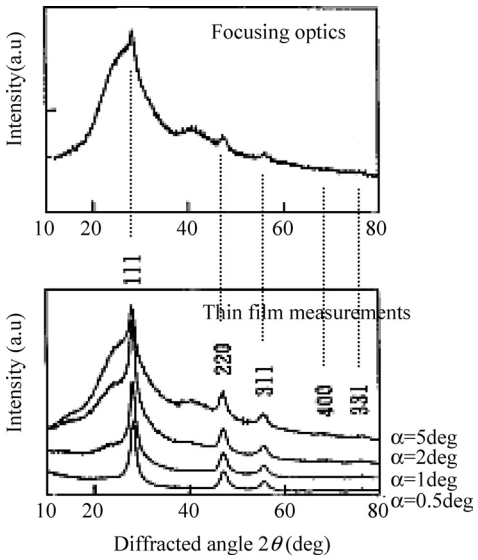

Fig. 9. XRD patterns for a silicon film on a glass substrate.

reflection measurements are shown in Fig. 9.

As shown at the top of Fig. 9, the diffraction pattern obtained by a symmetrical reflection measurement with focusing optics has strong scattering background (i.e., amorphous halo) from the glass substrate, and very weak diffraction peaks from the polycrystalline Si thin film. The Si thin-film peaks can be detected as overlapped on huge amorphous halo. As shown in the bottom of Fig. 9, the relative intensity ratio of the amorphous halo over the Si thin-film diffraction peaks decreases with decreasing incident angle α. The amorphous halo is practically invisible and only diffraction peaks from the film are visible when the incident angle α was reduced to 0.5°.

4.2. Copper wiring thin film on Si substrate

The diffraction patterns obtained by the symmetrical-reflection and the rocking-curve measurements for a copper wiring thin film (thickness 100 nm) deposited on a single-crystal Si substrate are shown at the top of Fig. 10. As discussed above, the symmetrical-reflection measurement provides crystallographic information perpendicular to the sample surface (or the stacking direction). X-ray diffraction patterns for randomly oriented Cu and Si powders as references, are also plotted at the lower parts of Fig. 10. There are two very strong peaks, i.e. the Cu(111) peak from the film and the Si(400) peak from the substrate, in the diffraction pattern of the thin-film sample (see the top pattern in Fig. 10). This indicates that the Cu film has a strong [111] texture.

The atomic arrangement of copper crystal is of the face-centered cubic (*fcc*) packing in which atoms are arranged to form a closest packing in (111). It is commonly known that thin films of these *fcc* materials show a [111] preferred orientation (or texture) as a result of minimization of the sum of the surface energy of crystals. The data shown in Fig. 10 confirms the [111] texture in Cu thin film with the symmetrical-reflection measurement. Since it is also important to evaluate the degree of preferred orientation for the [111] texture in this Cu film, a rocking-curve measurement was also performed. The rocking curve for the Cu(111) peak is shown in the top center of Fig. 10. The degree of orientation was evaluated from the full width at half maximum (FWHM) of the rocking curve. The FWHM of the rocking curve was determined to be 3.5°.

A thin film with preferred orientation is commonly analyzed by a combination of symmetrical-reflection and rocking curve measurements. Both measurements can easily be performed with the use of parallel-beam optics.

5. Concluding remarks

This article describe the principle, optics and the applications of the out-of-plane diffraction technique to

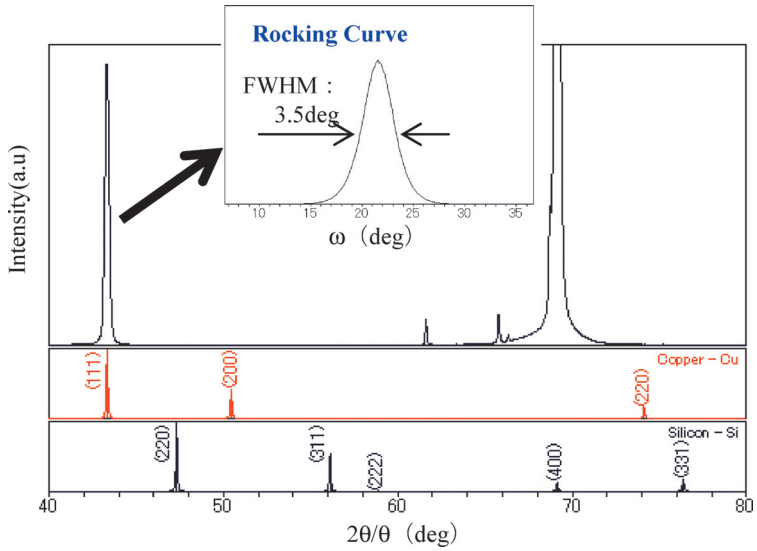

Fig. 10. Diffraction pattern and Cu(111) rocking curve for Cu wiring film on Si(100) substrate (top), powder diffraction pattern for Cu (middle; shown in red line), and Si (bottom; shown in dark blue line).

studying of thin films. This technique can be used to obtain crystal-structure information perpendicular to the sample surface (or the stacking direction). For structure information parallel to a sample surface, in-plane diffraction technique is used.

Other thin-film measurement techniques will be described in forthcoming articles in this series of "X-ray thin-film measurement techniques".

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