X-ray thin-film measurement techniques

I. Overview

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1. Introduction

There is a flood of high-tech functional devices made up of thin films. Cell phones and personal computers are integrated units of thin film devices, so are TV displays, recording media such as CD/DVD, their write/playback apparatuses, etc. X-ray measurement techniques are widely used for characterizing various thin-film materials and devices.

When a sample is "thin film," there are precautions and constraint conditions, characteristics for a thin film. For example, when a thin film has a strong preferred orientation, only one set of specific lattice planes can be detected. This is one of the reasons why measurements of thin films are more difficult compared with that of a powder sample. This article will overview this series for the basic techniques for X-ray characterizations of thin films.

2. Why thin film material is characterized using X-ray techniques?

2.1. Features of X-ray analysis

As the development of manufacturing technology of thin-film materials advances, the level and contents of analytical techniques used to characterize thin-film materials become more diversified and sophisticated. Among them, the progress of X-ray techniques for characterization of thin-film surfaces has been remarkable.

X-ray diffraction method as a tool for characterizing materials has a long history. It is one of the methods that have been successfully used for the determination of the crystal structure of a material. Although the X-ray diffraction method is a well-known technique, the method should be used after fully recognizing the differences from other evaluation methods and the feature of the method. When comparing to the electron beam diffraction method, the merits of the X-ray diffraction method are as follows.

- Non-destructive and no special sample preparation is required.
- Possible to be preformed in atmosphere and under a special atmosphere such as a high-temperature or high-pressure condition.
- Possible to obtain information on the average structure in a relatively large area (mm to cm).
- Irradiation damages in organic materials are low.
- Possible to control the analysis depth by the incident angle onto the surface.
- Possible to characterize buried interface structure.

The last two points of merits are important for the evaluation of thin films.

2.2. Obtainable information

A thin-film sample is two-dimensionally formed on the surface of a substrate, and normally has a large anisotropy either parallel along the stacking (thickness) direction or in the in-plane direction (within surface plane). For this reason, people frequently discuss material properties and characteristics along two directions: the stacking direction and in-plane direction. Subjects often being discussed as typical examples of anisotropy are crystal structure, crystallinity and other properties of a thin film. These subjects also include lattice constants, lattice distortion, crystal orientation, crystallite size, etc. Furthermore, the subjects for analyzing a thin film often include crystalline phase peculiar to the thin film, the presence of a phase that is unstable in bulk state, distortion/relaxation in an epitaxial thin film, etc.

In addition, the X-ray reflectivity method can be used to determine various properties of a thin film, such as the thickness and density of the film. This method can be applied to the thin films composed of amorphous materials or multilayered stacks. Table 1 shows an outline of various kinds of information that can be obtained by diffraction methods, reflectivity measurement and small angle scattering method when using an X-ray diffrac-

Table 1. Characterization methods of thin film using an X-ray diffractometer.

Measurement method	Scan axis	Obtainable information
Out-of-plane measurement	2θ/ω	Phase identification Crystal structure
Thin film method measurement	2θ	Phase identification Crystal structure
In-plane measurement	2θχ/φ φ	Phase identification Crystal structure
Pole figure measurement	χ(α), φ(β)	Preferred orientation
Rocking curve measurement	ω, χ, φ	Preferred orientation Crystallinity
Reciprocal space map	2θ/ω, ω 2θχ/φ, φ	Crystallinity Epitaxial Orientation Distortion/relaxation of the film
Reflectivity measurement	2θ/ω	Film thickness, density, roughness
Small angle scattering method	2θ/ω	Particle/pore size

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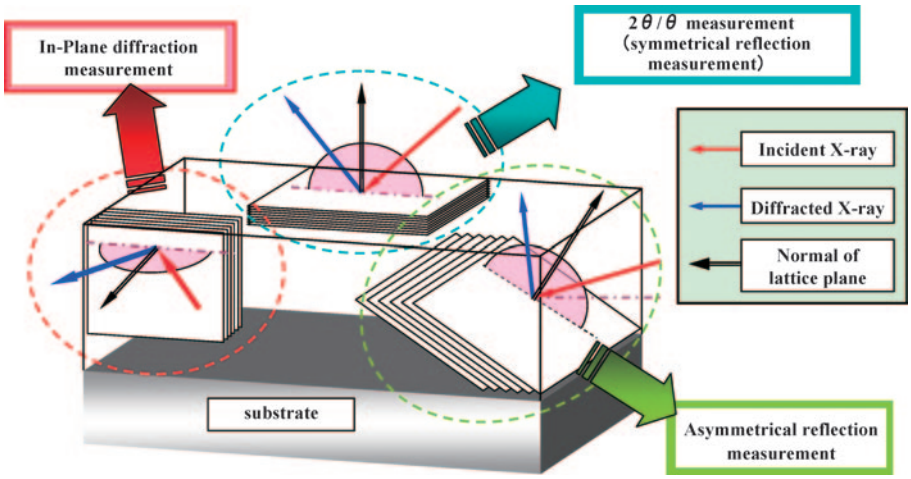

Fig. 1. Schematic diagram of geometries of various X-ray thin-film diffraction measurements.

tometer[1],[2].

2.3. Arrangements and geometries for X-ray measurements

As mentioned above, we can extract various kinds of structure and related information from a thin film. However, if X-rays are entered from the rear side of the substrate, normally it is difficult to detect X-ray signals. When we perform a $2\theta/\theta$ measurement on a powder sample using a conventional X-ray diffractometer, we can obtain only the information from lattice planes that are parallel to the sample surface. For this reason, when we measure a thin film sample, we must pay attention to the orientations of the lattice planes to be measured and the direction of the X-ray beam impinging onto the sample.

In a conventional $2\theta/\theta$ measurement, the measured lattice planes are parallel to the sample surface. The angles of the incident and the diffracted beams have the same angle (θ), and the measurement with this geometry is known as "symmetrical reflection measurement."

For a strongly preferred-oriented thin film, especially an epitaxial thin film, the information obtained by a $2\theta/\theta$ measurement is often not sufficient. Therefore, there is a need to measure lattice planes that are inclined to the sample surface. A thin-film measurement in which the incident angle of the X-ray beam impinging onto the surface is fixed to a shallow angle and only the detector is scanned to measure inclined lattice planes is known as "asymmetrical reflection measurement". Because in both the $2\theta/\theta$ measurement and the asymmetrical reflection measurement, the normal direction of the lattice planes goes out of the sample surface, these measurements are also called "out-of-plane measurement".

Isn't it possible to measure the lattice plane that is perpendicular to the sample surface? With improvements in measurement techniques and instruments in recent years, it is indeed possible to directly measure lattice planes that are perpendicular to the sample surface. In this case, because the perpendicular directions of these lattice planes to be measured lie parallel to the sample surface, the measurement is called "in-plane measurement." The in-plane measurement is extremely effective for characterizing a wide variety of thin films[3]–[7].

Figure 1 shows a schematic diagram of geometries for the three measurement techniques described above. We will explain these measurement techniques in details in the next and later parts of this article.

3. Instruments for X-ray thin-film measurements

3.1. Configuration

Generally an X-ray thin-film diffractometer that enables a wide variety of measurements is a complex instrument, which composes of various components including a measurement axis, sample position adjustment axes, optical elements, etc.

The instrument basically consists of the following five major components:

- X-ray source
- Incident optical system
- Goniometer
- Receiving optical system
- Detection section

The basic instrument is so called four-circle diffractometer that has been widely used in single-crystal structure determination. The diffractometer is generally composed of four axes: the ω axis (sample rotation axis), the φ axis (in-plane rotation axis), the χ axis (tilting axis) and the 2θ axis for scanning the detector.

The ω axis is also called as the θ axis in conventional X-ray diffraction measurements of powder sample. In a conventional powder diffraction measurement, the θ axis is controlled in conjunction with the 2θ axis so that its rotation angle is always being kept to a half of that of the 2θ axis. In an X-ray thin-film measurement, however, the sample rotation ω axis is generally controlled independent of the 2θ axis.

Since a measurement is performed mainly by scanning the ω axis and the 2θ axis, these two axes are called main axes. When high precision for a main axis is required, the smallest step of a rotation can be is one ten

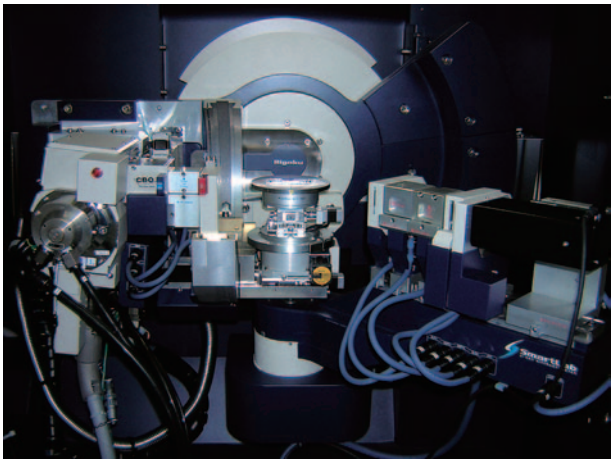

Fig. 2. X-ray thin-film diffractometer equipped with the $2\theta\chi$ axis (SmartLab).

thousandth of a degree (0.0001°). A high-precision measurement system with the smallest step of one hundred thousandth of a degree (0.00001°) in an ultrahigh precision measurement is commercially available.

In addition, to easily perform an in-plane measurement as described in the last half of Section 2.3, a five-axis diffractometer which has a fifth additional axis called "in-plane axis ($2\theta\chi$)" to scan the detector in the direction perpendicular to the 2θ axis is also commercially available (Fig. 2).

Other than the above scan axes, the following five additional axes are generally used for adjusting the position and/or orientation of a sample.

- "Z axis" (It adjusts the height of the sample surface to coincide with the center of the incident X-ray beam.)
- "X axis and Y axis" (They adjust the position of a sample surface on which X-rays are irradiated.)
- "Rx axis and Ry axis" (They adjust the normal axis of the sample surface to match the in-plane rotation axis (φ) in an in-plane measurement, in particular.)

3.2. X-ray optical geometries and optical elements

When measuring a thin film, an important factor that we must take into account is the selection of an X-ray geometry.

When we measure a thin film sample by means of the parafocusing X-ray geometry generally used for analyzing a powder sample, there is no big problem in performing a qualitative phase-identification analysis. However, for a quantitative analysis, it is not focused incident X-rays but parallel incident X-rays that are more suitable. For an optical element to parallelize the divergent incident beam that is emitted from an X-ray source, a multilayer mirror can be used[8]. An X-ray diffractometer in which the focusing and the parallel beam geometries can easily be switched without the need of changing its optical elements is commercially available (Cross Beam Optics™).

An epitaxial thin film in a compound semiconductive device is nearly perfect crystal. To characterize the crystallinity of such a thin film, an extremely small width

Fig. 3. Schematic diagram of monochromator crystals:
(a) 2-bounce monochromator
(b) 4-bounce monochromator

profile (generally called rocking curve measurement) obtained by a high-resolution measurement is required. In addition, a diffraction peak from a thin film may appear adjacent to a diffraction peak from the substrate, and a high-resolution measurement may also be required to separate and measure these adjacent peaks. A perfect single-crystal monochromator such as Si and Ge can be used to reach such high resolution. The incident X-ray beam after diffraction from a same set of lattice plane is highly parallel and monochromatic (for example, a CuKα_1 X-ray beam with wavelength of 1.54059 Å).

Figure 3 (a) and (b) show a schematic diagram of commonly used monochromator crystals. The thick black lines represent the X-ray beams and the blue blocks represent the monochromator crystals. The monochromators are channel-cut crystals so that the X-ray beam reflects twice in a single block of crystal. Because the directions of the X-ray incident beam and the exit beam from the monochromator are parallel, an alignment of the instrument is easy.

The resolutions for measuring a rocking curve using a two-bounce monochromator and a four-bounce monochromator are about 0.01° and 0.003°, respectively (note: resolution is dependent on the lattice planes employed). X-ray intensities of a four-bounce monochromator are smaller by about an order of magnitude than those of a two-bounce monochromator. Since there is a trade-off between resolution and intensities, we must select a monochromator by carefully taking into account all factors. An instrument manufactured for X-ray thin-film measurements having the capability of an automatic replacement of its monchomator with high-precision reproducibility is also commercially available. Since some components of an X-ray instrument such as its X-ray source may degrade by aging, therefore, in order to make sure the instrument is always under the best conditions, it is important that the instrument has a mechanism enabling the user to request an automatic adjustment by the computer.

To enhance the resolution of a diffracted beam, a channel-cut crystal before the detector similar to the one in the incident beam can be used. This receiving X-ray optical element is called analyzer crystal. The resolution produced by an analyzer crystal is better than or equal to 0.01°. However, if the requirement of the resolution is a little laxer to 0.1 or 0.5°, a mechanical receiving slit or PSA (Parallel Slit Analyzer) is used. The latter is an effective element for obtaining a constant resolution even for X-rays spreading over a wide area.

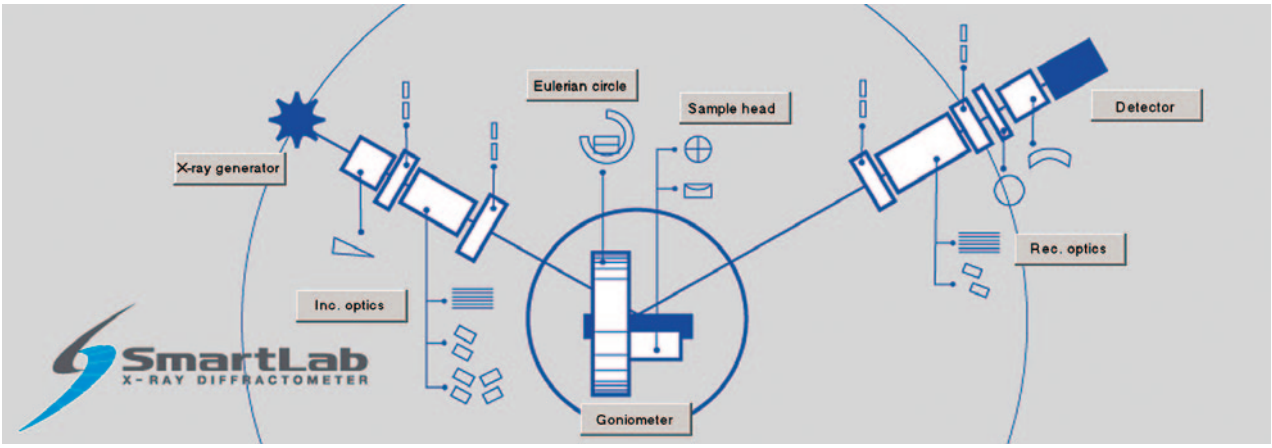

Fig. 4. Instrument configuration display screen of SmartLab Guidance.

3.3. Detecting section

For a device to measure intensities of the X-ray beam diffracted by a sample, a scintillation counter is widely used because of its high detection sensitivity, low noise level, and easiness for handling. A scintillation counter can measure X-ray intensities varying over large orders of magnitude from a lower counting rate of 0.1 count/sec up to a higher counting rate of a few 100 thousand count/sec after an automatic correction for possible count losses. When we use a high-intensity X-ray source or when the possibility of the X-ray intensity to exceed the detection upper limit of the detector is high, it is necessary to protect the detector by attenuating the diffracted X-ray intensities entering into a detector with metallic foils in front of the detector. The device to achieve this function is called attenuator. Attenuators composed of metallic foils are used in some modern X-ray thin-film diffractometers to automatically adjust the total thickness of the metal foils to obtain an optimum attenuation rate. It should be noted that a method to decrease the incident X-ray intensities by reducing the output power of an X-ray source should not be used because it can cause a subtle shift of the focus position of the incident X-ray beam, resulting a misalignment for the incident optical system.

Since a scintillation counter has no spatial resolution, it is classified as a point detector. In recent years, one-dimensional and two-dimensional detectors are also available.

3.4. Control software

As mentioned above, in an X-ray measurement of a thin-film sample, we need to use various optical elements, control several diffractometer axes, acquire measurement data by combining various measurement methods, and then analyze the acquired data. For this reason, control and measurement software is provided in one package, which includes automatic and independent adjustments of all components in the instrument including its X-ray optics, sample orientation and position, etc. (SmartLab Guidance).

A general configuration of devices for an advanced X-ray instrument displayed using the SmartLab Guidance is shown in Fig. 4. An automatic sensing of the device configuration is also included. The instrument will issue a warning if the actual device configuration is different from the one specified in the measurement screen, and instruct the user to choose a correct device configuration.

4. What kinds of measurements can be conducted?

A wide variety of thin-film materials and devices have been the subjects of research and development. These thin-film materials and devices can be grouped and classified in according to their structures, chemical and physical properties. Table 2 shows a classification table of various materials that have been characterized by the author.

In the process of research and development of epitaxial thin films, the characterizations of lattice distortion, degree of relaxation and the composition of solid solution (mixed crystal), etc. are often conducted.

For the research and development of polycrystalline thin films, qualitative X-ray analysis is commonly used first to identify what crystalline phases have been produced. Next, the actual material composition and layer configuration are determined. Finally determinations of degree of preferred orientation, lattice distortion, crystallite (or particle) size, etc. are the keys for the characterization.

This table is a summary based on my works so far, and it surely should be updated with new developments of thin film manufacturing technologies and device applications.

5. Concluding remarks

As described above, I have given a brief overview of X-ray thin-film measurement methods. In future articles, we plan to give detailed descriptions on important features, characteristics, methods of thinking for X-ray thin-film measurements, and these will include out-of-plane measurement, high-resolution X-ray diffraction measurement, reflectivity measurement, in-plane mea-

Table 2. Measurement examples for various materials.

Class		Major material	poly crystalline ← X-ray diffraction measurement → single crystalline							Reflectivity measruement		Small angle scattering
			Phase ID	crystallite size	orientation	lattece strain	composition (solid solution)	lattice constant, crystallinity	relaxation	thickness, roughness	density	pore/particle size distribution
Semiconductor epitaxial film	Ⅳ-Ⅳcompound	Si, SiGe, SiC...	–	–	△	–	◎	◎	◎	◎	○	–
	Ⅲ-Ⅴcompound	GaAs, AlGaAs, InP...	–	–	△	–	◎	◎	◎	◎	○	–
	Ⅲ-N compound	GaN, AlN, InN, BN...	△	–	○	△	◎	◎	◎	◎	○	–
	Ⅱ-Ⅵcompound	ZnO, ZnSe...	△	–	○	△	△	○	○	△	△	–
	others	$FeSi_2$...	△	△	◎	△	△	△	△	△	△	–
semiconductor poly-film		poly-Si, μc-Si...	–	○	◎	○	–	○	–	◎	◎	–
semiconductor amourphous film		a-Si, a-SiN...	–	△	–	△	○	–	–	◎	◎	–
barrier film		Ta, TaN, Ti, SiN...	○	○	△	○	◎	△	–	○	○	–
electrode -interconnect-		Cu, Al...	△	○	◎	○	△	△	–	○	○	–
electrode	cotact	$CoSi_2$, NiSi, W, Pt, Ir...	◎	○	◎	○	△	△	△	○	○	–
	TCO	ITO, ZnO, CdO...	○	○	◎	○	△	△	–	○	○	–
low-k			–	–	–	–	–	–	–	◎	◎	◎
high-k		ZrO2, HfAlOx, SiON...	◎	○	△	○	○	–	–	◎	◎	–
Ferroelectric film		PZT, SBT, BST, AlN...	◎	△	◎	○	◎	△	△	○	○	–
coating film		DLC...	–	–	–	△	△	–	–	◎	◎	–
organic film		small molecular material, polymers	○	○	○	△	–	△	–	○	○	–
magnetic film	media	Co, CoCrPt...	○	○	○	○	△	○	–	◎	○	–
	next generation	FePt, CoPt, granular...	○	○	◎	○	△	○	–	○	○	◎
	head	NiFe/Ta...	○	○	△	○	○	△	–	◎	◎	–
	others	MnGaAs, Fe-epi...	△	○	◎	○	○	○	○	◎	◎	–
piezoelectric material		LN, LT, SiO_2, Langasite, AlN, BBO...	△	–	○	○	○	◎	–	△	○	–
super conductor		YBCO, La_2CuO_4, MgB_2...	○	○	◎	○	○	○	○	△	△	–
substrate		Si, GaAs, Sap, SiC, ZnO, YSZ, STO, LSAT...	△	–	△	○	△	◎	–	△	–	–
bulk		composite subst(ITO/GI)、UV window(CaF_2, BaF_2)	△	△	○	–	–	–	–	△	△	–
nano material		nano particle, phonic material, mesoporous material	–	△	△	△	–	○	–	○	○	◎

Legend symbols : ◎Frequently evaluated, ○ often evaluated, △ occasionally evaluated, – seldom evaluated

surement, small-angle scattering measurement, pole figure measurement, etc.

References

(1) D. K. Bowen and B. K. Tanner: "High Resolution X-ray Diffraction and Topography", Taylor & Francis Inc. (1998).
(2) L. G. Parratt: *Phys. Rev.*, **95** (1954), 359.
(3) K. Omote and J. Harada: *Advances in X-ray Analysis*, **43** (2000), 192–200.
(4) T. Yamada, A. Miyake, S. Kishimoto, H. Makino, N. Yamamoto and T. Yamamoto: *Appl. Phys. Lett.*, **91** (2007), 051915-1–051915-3.
(5) M. Ofuji, K. Ishikawa, H. Takezoe, K. Inaba and K. Omote: *Appl. Phys. Lett.*, **86** (2005), 062114-1–062114-3.
(6) A. Takase, G. Fujinawa, A. Ebina, M. Hirasaka and I. Sugiyama: *Jpn. Jour. Appl. Phys.*, **41** (2002), 2189–2190.
(7) Y. Ito, K. Inaba and K. Omote: *Jour. Phys.: Conf. Ser.*, **83** (2007), 012015-1–012015-4.
(8) L. Jiang, Z. Al-Mosheky and N. Grupid: *Powder Diffraction*, **17** (2002), 81–93.