X-ray thin-film measurement techniques

III. High resolution X-ray diffractometry

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1. Introduction

Recently, there are a very large number of electric devices developed in the high-tech industry. Semiconductor material is one of the basic components for these electronic devices. For example, III–V compounds (GaN, GaAs, etc.) are often used to produce optical devices because the band gap range of these compounds are close to the visible light range. These compounds can coordinate band gap making a solid solution with another III–V compound. For instance, GaN can adjust the luminescence wavelength and the refractive index by making solid solution with In or Al. As a result, these compounds can be applied to electronic devices such as blue light emitting diodes, semiconductor lasers, etc.

In the development of these materials, it is important to obtain the correlation between device performances and their physical properties. X-ray diffraction method is commonly used to obtain information about physical properties, including composition and thickness of a thin film and orientation relationship between the film and its substrate.

Two of the most basic semiconductor components in many electronic devices are an epitaxial film and its perfect single-crystal substrate. X-ray dynamical theory can be used to study perfect single-crystal materials. The dynamical diffraction theory is different from conventional X-ray diffraction theory used for the studying of a polycrystalline sample as well as an imperfect crystal. To apply this theory, the conventional X-ray powder diffraction method, which is used for studying polycrystalline samples, is not sufficient, and the high-resolution X-ray diffraction method is required.

In this article, high-resolution diffraction method mainly used for the characterization of semiconductor materials and single crystal substrates is explained.

2. X-ray diffraction measurement and reciprocal vector

It is very useful a common practice in crystallography to represent a set of crystal lattice plane (*hkl*) by a vector. The vector is a physical quantity containing a length and a direction. For a set of lattice planes (*hkl*), the length and the direction of the vector is defined as follows:

– Length: inverse of *d*-spacing of a set of the lattice planes (*hkl*)
– Direction: perpendicular to the (*hkl*) lattice planes.

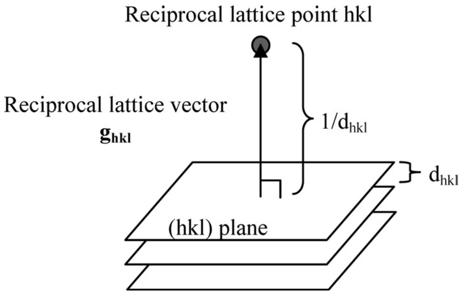

Fig. 1. Reciprocal lattice vector and reciprocal lattice point of a set of the lattice planes (*hkl*).

This vector is called the reciprocal lattice vector ($\mathbf{g}_{hkl}$), and the end point of the vector is called the reciprocal lattice point (*hkl*). If changes in lattice constants and/or the direction of the lattice planes occur, the length and direction of g_{hkl} will also be accordingly. The size and/or the shape of a reciprocal lattice point can be affected by the crystallinity and/or the anisotropy presented in a sample. The reciprocal lattice mapping measurement (Section 4.2) can be used effectively for this type of study.

Next, let us consider the diffraction condition. The incident and scattered (or diffracted) X-ray beams are represented by the wave vectors $\mathbf{k}_0$ and $\mathbf{k}$, respectively, as follows:

$$\mathbf{K}=\mathbf{k}-\mathbf{k}_0 \tag{1}$$

Where $\mathbf{K}$ is the scattering vector and its length $|\mathbf{K}|$ equals to the inverse of lattice spacing, d_{hkl} (Fig. 2).

If the incident angle and the exit (or diffracted) angles are kept equal and only the scattering angle is changed, the scattering vector will also change as shown in Fig. 2.

In a conventional θ–θ scan, the incident angle and the exit angle are kept equal during a scan, and this

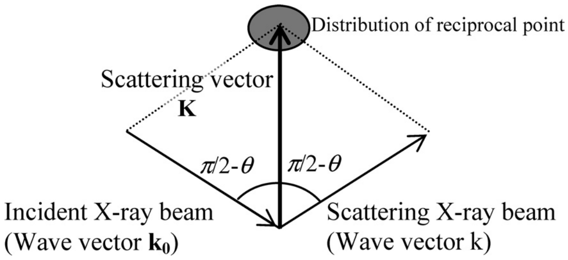

Fig. 2. Vector notation of X-ray diffraction condition.

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corresponds to changes in the directions of $\mathbf{k}_0$ and $\mathbf{k}$. As a result, the length and the direction of the scattering vector $\mathbf{K}$ is also changed. When the scattering vector $\mathbf{K}$ equals to the reciprocal lattice vector $\mathbf{g}_{hkl}$, the diffraction condition, i.e. the Bragg equation, is satisfied.

3. High resolution X-ray diffractometry

3.1. Kinematical and dynamical diffraction theories (1), (2)

Powders and the imperfect crystals generally have lattice defects, such as dislocations, and their three-dimensional periodicity tends to be imperfect. A mosaic crystal models this imperfection as an assembly of a large number of minute regions, without disorders in periodicity, but with slight differences in orientations. Because a mosaic crystal has small domains, the incident X-ray beam is scattered by each domain independently (Fig. 3). The kinematical diffraction theory has been used successfully to study many inorganic and organic crystals, as well as amorphous and liquid materials.

On the other hand, if a crystal is nearly perfect, which is different from a mosaic crystal, the effect of multiple scattering can not be neglected as shown in Fig. 4. The theory that multiple scattering phenomena are taken into account is called dynamical diffraction theory. This theory holds for the cases of perfect crystals such as Si, Ge, GaAs, GaN. As Fig. 4 shows, if the X-ray wave in the incident direction (or transmission direction) is scattered by a lattice plane in a perfect crystal, waves are generated in both the diffraction direction and the transmission direction. These waves reflect repeatedly by many lattice planes. When such reflections are repeated, various diffraction phenomena arise due to interference (or interaction) between the diffracted and the transmitted waves within the crystal.

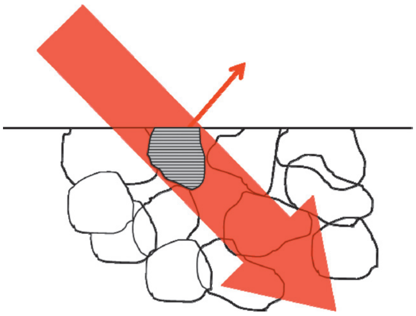


Fig. 3. Kinematical diffraction.

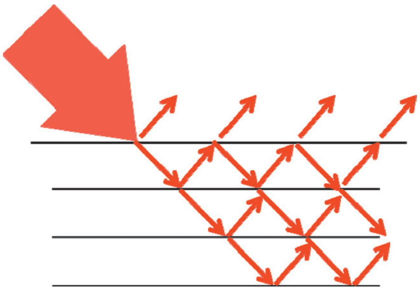


Fig. 4. Dynamical diffarction.

3.2. Incident optics

In a compound semiconductor material, the solid solution may be made from two or more compounds to control the band gap of the material. The composition of the solid solution can be obtained from the measured value of lattice constant using Vegard's law. For example, AlAs and GaAs each has a band gap and a lattice constant characteristic of the compound. However, a ternary semiconductor $Al_xGa_{1-x}As$, a mixed crystal of these two compounds, will have a lattice constant in between those of AlAs an GaAs. The value of the lattice constant of $Al_xGa_{1-x}As$ can be calculated from Vegard's law and the value of x. The lattice constants of GaAs and AlAs are:

$$a_{\mathrm{GaAs}}=5.6538\,\text{Å}$$

$$a_{\mathrm{AlAs}}=5.6611\,\text{Å}$$

The difference in the lattice constants, Δa, is only $0.0073\,\text{Å}$ or $\Delta a/a=1.3\times10^{-3}$. To determine the composition to a precision of 1%, the lattice constant must be determined to 1/100 of this precision. This corresponds to measuring the Bragg angle at a precision on the order of several ten-thousandths of a degree. This precision is more than an order of magnitude greater than the precision obtained by a conventional powder diffractometer. Therefore, a high-resolution X-ray diffractometer equipped with a multiple-crystal monochromator is required. A multiple-crystal monochromator is an X-ray optical device that uses the diffraction phenomenon generated by a perfect single crystal to monochromate and collimate the incident X-ray beam.

The crystal used to monochromate and collimate the incident X-ray beam is commonly made from a perfect single crystal of Ge or Si. Figure 5 shows the variations of crystals and optics using for the high-resolution X-ray diffraction method. The monochromators are channel-cut crystals so that the incident X-ray beam reflects twice in a single block of a crystal. The channel-cut crystal is a single-crystal block in which a channel is cut, with a structure consisting of two facing single crystals. Figure 5 shows examples of using Ge single crystals, and Si crystals can also be used.

Table 1 shows the relationship among resolution (angular divergence), monochromaticity of wavelength and relative intensity. As expected, an optical device with higher resolution has higher precision. However at the same time, it gives lower incident and diffracted X-ray intensities, and this prolongs the measurement time. The intensity diffracted by a Ge (220) 4-bounce crystal is almost 1/100 of that using a slit collimation geometry. Please notice that if you want to have high resolution, then the intensity will be sacrificed.

When measuring a sample with undetermined crystal perfection, it is better to first use the slit collimation geometry to obtain the highest possible intensity from

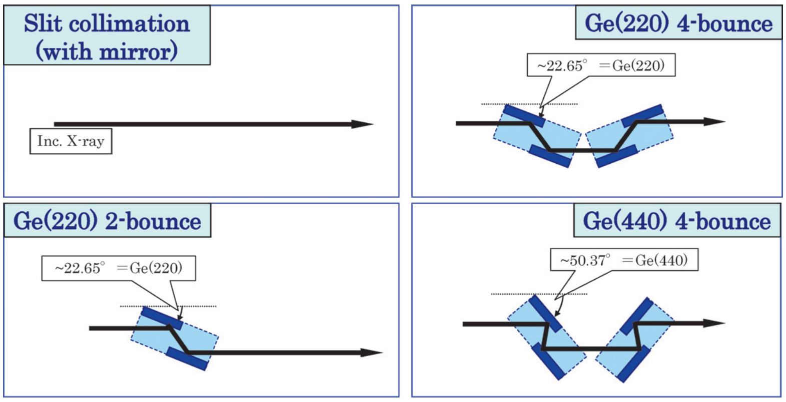
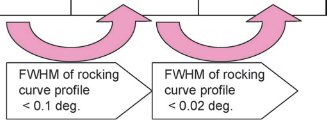


Fig. 5. Example of incident optics for high-resolution diffractometry.

Table 1. Function and selection of optical devices.

Optics	Slit collimation	Ge(220) 2–bounce	Ge(220) 4–bounce
Resolution	0.05 deg.	0.01 deg.	0.0033 deg.
Monochromaticity of wavelength	K α_1 + α_2 (+Kβ)	K α_1	Part of K α_1
Relative intensity	1	1/20	1/100



a weak diffraction peak. Next, a rocking curve measurement (or ω measurement) is performed by rocking the thin-film sample while the detector is fixed at a fixed 2θ angle to record diffraction intensities to check the full width at half maximum intensity (FWHM) of the peak. If the FWHM of the peak is less than 0.1 degree, it is necessary to change to a Ge (220) 2-bounce crystal because the slit collimation has insufficient resolution. A similar measurement is then performed after changing the optics, and if FWHM of the peak is less than 0.02 degree, it is again necessary to change to a Ge (220) 4-bounce crystal to get even higher resolution.

The resolution of a monochromator is a function of the Bragg angle, θ_B, of the measured sample, and the relationships between the Bragg angles and the resolutions of commonly used Ge monochromators are plotted in Fig. 6. The angular divergences (or resolution) of both Ge 2-bounce monochromators each reach a minimum (and thus the angular resolution in a diffraction measurement reaching a maximum) when the Bragg angle of the channel-cut crystal equals to the Bragg angle of the measured sample. The Bragg angle is θ_B=22.6° for Ge (220) and θ_B=33.0° for Ge (440). Each of the two Ge 4-bounce monochromators has high resolution over a wide diffraction angle range. Here, a channel-cut crystal with higher Miller indices can provide better monochromaticity and collimation. Comparing the Ge (400) 2-bounce with the Ge (220) 4-bounce crystals, the Ge (220) 4-bounce crystal can give high resolution over a wide diffraction angle range. On the other hand, the Ge (400) 2-bounce crystal can provide higher resolution than that of the Ge (220) 4-bounce crystal at θ~33.0 degree.

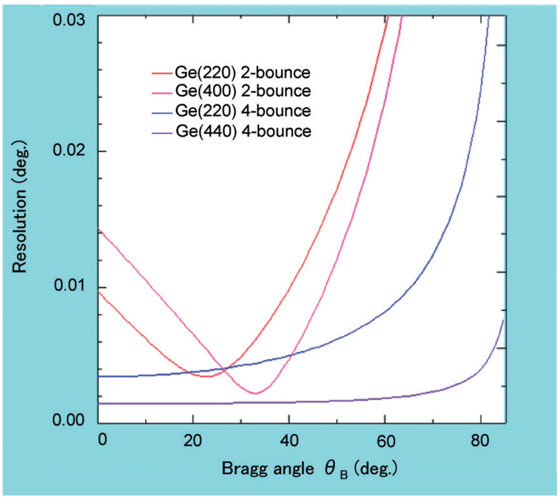


Fig. 6. Monochromators and their resolution.

Figure 7 shows the X-ray diffraction results between 65.85 and 66.15°2θ using three different channel-cut Ge crystals. In the case of using a Ge (400) 2-bounce crystal, high resolution almost the same as that obtained by a Ge (440) 4-bounce crystal was obtained. Both diffraction curves have fine oscillations arising from the thickness of the AlGaAs film. However, the diffraction intensities obtained by using the Ge (400) 2-bounce crystal are almost 100 times larger than those obtained by the Ge (440) 4-bounce crystal. This is an example

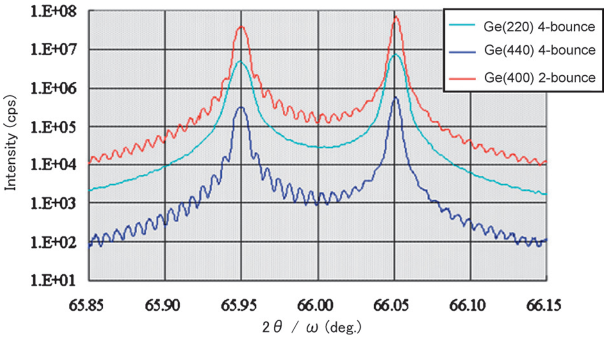


Fig. 7. Rocking curve profiles of AlGaAs/GaAs with various incident optics.

that good quality data with high intensities and high resolution can be obtained by selecting an optimum monochromator crystal most suitable for the diffraction angle of the sample.

Figure 7 also shows that the diffraction curve obtained by using a Ge (220) 2-bounce crystal has poor resolution with no detectable oscillations. Because there are no observable oscillations, this diffraction curve cannot be used to determine the thickness of the AlGaAs film.

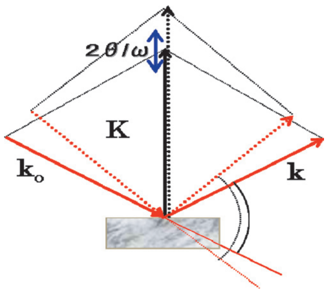


Fig. 8. Rocking curve measurement.

4. Measurement and analysis

4.1. Rocking curve measurement ($2\theta/\omega$ scan)

In general, "rocking curve measurement" may signify the technique which is performed by rocking a thin-film sample while the detector is fixed at a certain 2θ angle to measure diffraction intensities from the lattice planes for the determination of the degree of preferred orientation presented in the sample. In the meantime, a $2\theta/\omega$ scan used for the study of an epitaxial film grown on a single-crystal substrate is also called "rocking curve measurement". In this article, rocking curve measurements were performed by $2\theta/\omega$ scan.

4.1.1. Measuring method

In the case of a rocking curve measurement, $2\theta/\omega$ is used for measurement axis same as the out-of-plane method. The incident angle and the exit angle are kept equal during a $2\theta/\omega$ scan (Fig. 8).

In the $2\theta/\omega$ measurement, the direction of the scattering vector **K** is fixed, and only the length of **K** is changed. If the measured lattice planes are parallel to the sample surface, the incident X-ray beam is diffracted by the lattice planes, which direction matches the scattering vector.

In a rocking curve measurement, it is necessary to adjust the tilting axis for an existing reciprocal lattice point on the scattering plane, which contains the incident X-ray beam and the diffracted X-ray beam. This operation is termed a tilting axis adjustment. Almost all modern XRD systems have automatic tilting-axis alignment software programs.

Figure 9 shows the effect of a misalignment of a tilting axis on an ω scan. The profiles expressed in the figure are results of an ω scan while gradually changing the tilting angle. The aligned position of the tilting axis is located at the lowest peak position, the smallest FWHM of the peak, and strongest intensity peak position.

To place the reciprocal lattice point in the scattering plane, adjust the χ axis for a symmetric reflection and the ϕ axis for an asymmetric reflection. Figure 10 shows the change in the incident angle following a shift in the tilting angle. If the tilting angle is not properly adjusted, the position of the diffraction peak will shift to the higher angle side of the correct position, the peak width will spread, and the intensity of the diffraction peak will be weak.

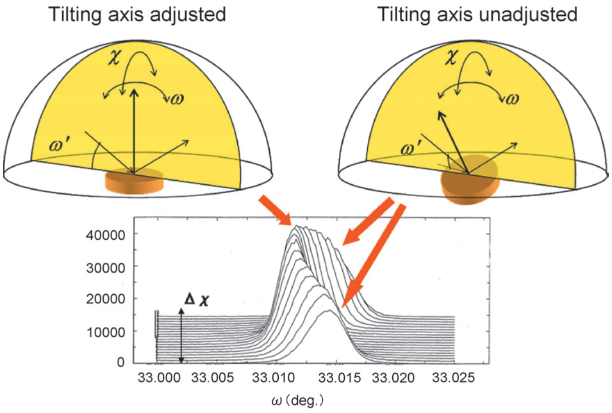


Fig. 9. Effect for ω scan by misalignment of tilting axis.

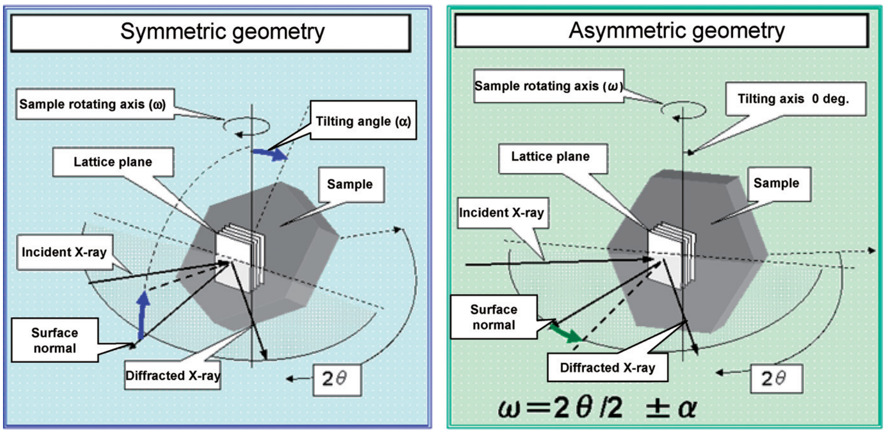


Fig. 10. Symmetric geometry and asymmetric geometry.

4.1.2. Analysis and interpretation of profiles

Figure 11 shows a rocking curve profile of an $In_xGa_{(1-x)}As$ (x=0.01) epitaxial film of 200 nm thick grown on a (001) GaAs substrate.

The (004) peak of $In_xGa_{(1-x)}As$ is observed at the low-angle side of the GaAs (004) peak (see Fig. 11). In the case of a material in a solid solution system, its lattice constant changes systematically with its composition.

From the shift of the diffraction peak of a film related to its substrate, we can calculate the lattice constant of the film if the lattice constant of the substrate is known. If the presence or absence of lattice relaxation and the elastic constant of a film are known, we can use the calculated lattice constant to determine the composition ratio of the mixed crystal in the film (in this example, the ratio of InAs and GaAs) based on Vegard's law. Additionally, the diffraction intensities oscillate on both sides of the diffraction peak of the film. We can obtain the thickness of the film based on the period of this oscillation. In some case, the lattice constant of thin film layer is distorted because lattice miss-match. In such a case, a confirmation of lattice distortion condition using a reciprocal space mapping measurement is needed.

Figure 12 shows the change of rocking-curve profiles of two $In_xGa_{(1-x)}As$ films with x=0.010 and 0.012. The peak position of $In_xGa_{(1-x)}As$ is shifted to a lower angle.

If you just want to know the film thickness, it can be calculated from the peak position and the interval of neighboring oscillation peaks (fringes).

Figure 13 shows the change of profiles due to 2 different film thicknesses. The thicker the film, the shorter the oscillation.

The profile fitting technique is commonly used for this type of analysis. The thickness and the composition of a multilayer film cannot be determined directly from a measured rocking curve profile. In an actual analysis, we must simulate a rocking curve from a multilayer-film model with hypothetical film thicknesses and compositions and change the thicknesses and the compositions to match the measured rocking curve in the analysis.

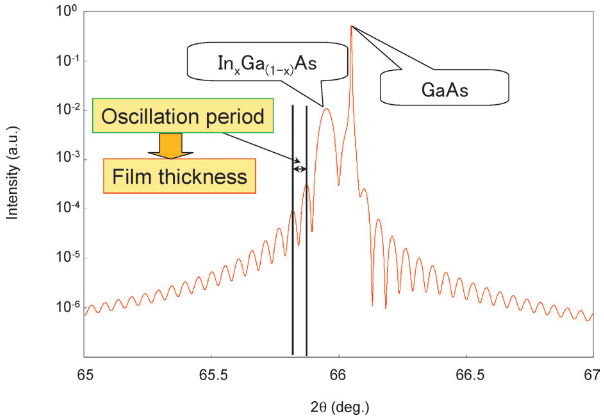


Fig. 11. Rocking curve profile of $In_xGa_{(1-x)}As/GaAs$.

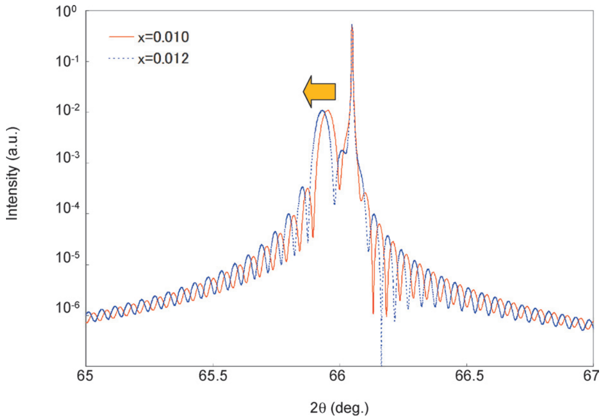


Fig. 12. Rocking curve profiles of $In_xGa_{(1-x)}As/GaAs$ (changes of profiles due to the difference in composition).

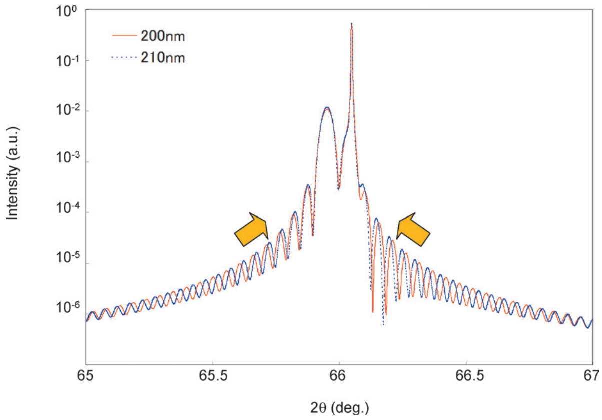


Fig. 13. Rocking curve profiles of $In_xGa_{(1-x)}As/GaAs$ (changes of profiles due to 2 different film thicknesses).

In the past, the main function of an application software was to conduct least-squares fitting. As a result, the fitting parameters were easily diverged, unless the designed parameters in the starting model were very close to the true values.

Nowadays, the "Global optimization" technique is commonly used. This technique can obtain the true answers even if the designed values are far from the true values. This method is also very powerful for analysis of a thin film with a complicated structure. The "Global optimization" is significantly different from least-squares fitting. In the calculation using least-squares fitting, the parameters can only be optimized in a local domain. On the other hand, the parameters are optimized in the global domain using "Global optimization".

Figure 14 shows a screen image of the integrated thin film analysis software GlobalFit (Extended Rocking Curve Analysis), which can perform many useful functions. In this software, constructions of initial structure, profile simulation, global optimization, least-squares fitting, an analysis of a multilayer thin film, periodic layer structure and slope of composition can easily be done.

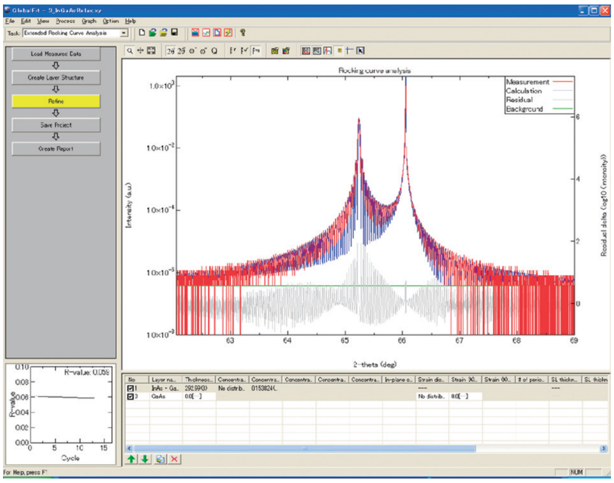


Fig. 14. A screen shot of the "GlobalFit" software.

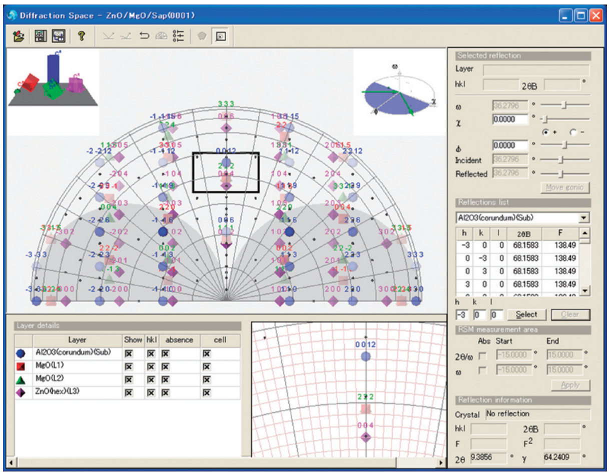


Fig. 16. A view of "Diffraction Space Simulation" software for reciprocal lattice simulation.

4.2. Reciprocal space mapping measurement

4.2.1. Measuring method

As shown in Fig. 15, the reciprocal lattice point spreads caused by changes in crystal structure or degradation in crystallinity can be attributable to changes or spread in the crystal orientation or the lattice constants.

The reciprocal space mapping measurement records diffraction intensity distributions by scanning both the diffraction angle and sample rotation axes, and plots the result in the reciprocal space. The reciprocal lattice map can provide information on the crystal structure, crystal orientation relationships, crystallinity, and the preferred orientation of the sample investigated. The central coordinates, shapes, and positional relationships of the reciprocal lattice points appearing in a two-dimensional (or three-dimensional) data plotted in the reciprocal space provide a wide range of information on crystal structure. So, this is the method which obtains two dimensional distribution maps with the scanning scattering vector **K** (Fig. 15). The distributions of the directions and intensities of reciprocal points perpendicular to the sample surface are observed using the in-plane measurement method instead of using the out-of-plane measurement.

To combine these two methods, distributions of reciprocal points can be observed three dimensionally and the orientation relationships between a thin film and its substrate. Lattice constants and the condition of strain can be analyzed from the information of the positional relationships and the shape of reciprocal points.$^{(3)-(8)}$

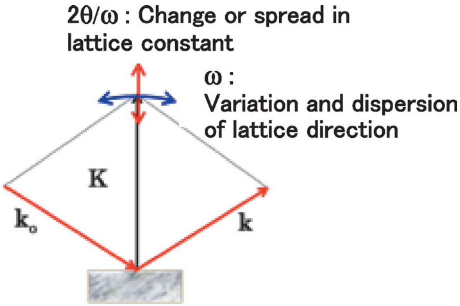


Fig. 15. Reciprocal space mapping measurement.

If you want to measure a reciprocal space map, it is necessary to examine the relationship of crystal orientation directions between a thin film and its substrate as well as the diffraction angle based on the designed values. The position of reciprocal lattice points can calculate based on crystal structure information. In this calculation, crystallographic knowledge is needed. On the other hand, the information are obtained only by selecting the structure of a thin film because the "SmartLab Guidance" software has the function of reciprocal lattice simulation named "Diffraction Space Simulation (DSS)" software (Fig. 16). This software can calculate the positions of the goniometer axes to catch signals from the corresponding reciprocal lattice points.

4.2.2. Analysis and interpretation of data

Figure 17 shows the results of the reciprocal lattice mapping measurement of an AlGaAs thin film on a GaAs substrate. The reciprocal map shows that the thin film layer is fully strained. The AlGaAs lattice is constrained to the GaAs substrate lattice so that the

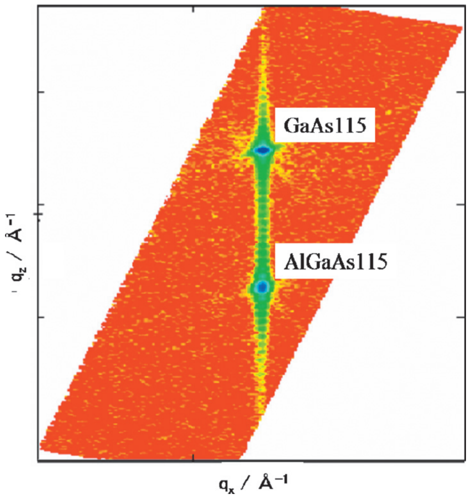


Fig. 17. Reciprocal space map of AlGaAs on GaAs.

reciprocal lattice points of the film and the substrate are lined in the vertical direction (the q_z axis in Fig. 17), and these lattices have the same length in the horizontal direction (i.e., the q_x axis). It is very useful to express the positions and shapes of reciprocal lattice points using the Cartesian coordinates system (i.e., q_x, q_y) instead of 2θ and ω for calculating the d-spacings. This conversion can be done following the simple formula shown in equation (2). In Fig. 17, the vertical axis and the horizontal axis are shown using reciprocal space coordinates. Figure 18 shows the concept of a reciprocal space map and q coordinates. In Fig. 18, the lattice plane parallel to the sample surface is (00l).

$$q_x = \frac{2}{\lambda}\sin\frac{2\theta}{2}\sin\left(\frac{2\theta}{2}-\omega\right) = \frac{1}{\lambda}\left\{\cos\omega - \cos\left(2\theta-\omega\right)\right\}$$
$$q_z = \frac{2}{\lambda}\sin\frac{2\theta}{2}\cos\left(\frac{2\theta}{2}-\omega\right) = \frac{1}{\lambda}\left\{\sin\omega - \sin\left(2\theta-\omega\right)\right\} \tag{2}$$

In some cases, equation (2) is calculated multiplying 2π. Both q_x and q_z are the inverse of lattice spacing and are also expressed as $q_{//}$ and $q_{\perp}$ because of the position relationships of the sample surface normal. For example, q_z is parallel to crystal direction axis of the sample [001], and q_x is parallel to [hk0] as shown in Fig.18. In this instance, d_{hk0} and d_{001} are calculated from the central coordinates of reciprocal lattice point distribution (q_x, q_z), and from that the lattice constants can be calculated.

The relative positions of the reciprocal lattice points of an epitaxial film and its substrate change, depending on lattice matching and the presence or absence of lattice relaxation. Figure 19 schematically illustrates the reciprocal space maps for relaxed, strained and misoriented films. The term lattice relaxation refers to the state of an epitaxial film having the same cubic crystal structure as the bulk of the material composing the film, as shown in Fig. 19(a). In this case, the reciprocal lattice point of the film with the indices (hkl) is positioned on the line connecting the reciprocal lattice point (hkl) of the substrate and the origin of the reciprocal lattice—along the line of the $2\theta/\omega$ scan for both symmetric and asymmetric diffractions.

If the lattice of the film is strained at the interface between the epitaxial film and the substrate in a manner such that the in-plane lattice constants of the epitaxial film and substrate match, the reciprocal lattice point of the film with the indices (hkl) is positioned directly below the reciprocal lattice point (hkl) of the substrate for both symmetric and asymmetric diffractions (see Fig. 19(b)). In the case for asymmetric diffraction, the reciprocal lattice points of the substrate and the film are not positioned on the same line of a $2\theta/\omega$ scan. If crystal orientation direction of thin film is tilted with respect to the substrate, the reciprocal lattice point of thin film is also tilted as shown in Fig. 19(c).

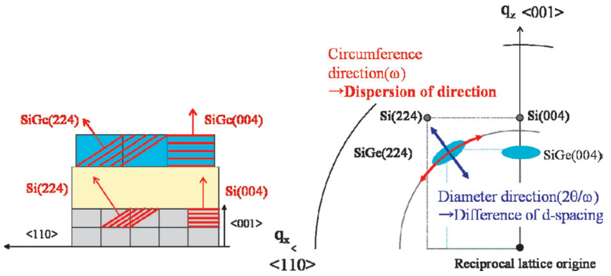


Fig. 18. Concept of reciprocal space map and q coordinates.

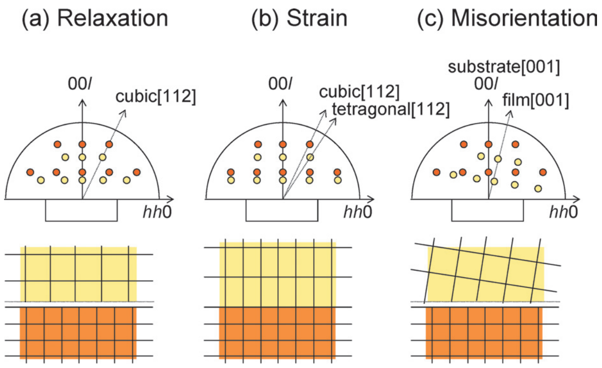


Fig. 19. Reciprocal space maps of hetero epitaxial layer.

4.2.3. Precaution of measurement

The technique for high-resolution measurements has been described in the previous section. However, we should also be careful about the resolution of the receiving optical system. The relationship between reciprocal lattice points and optical resolution is shown Fig. 20.

If the resolution of the incident or receiving optics decreases, the scattering in a region in the reciprocal space increases accordingly. When this happens, even if the true reciprocal lattice point is extremely small, the reciprocal lattice point is observed with a spread corresponding to the resolution. The region in which the scattering is observed is called the resolution function. The size and shape of the resolution function depends on the optics used in a measurement. As discussed in the previous section, the size and shape of the resolution function are related to the resolution of the optics (see also Fig. 20).

A preliminary measurement without using an analyzer crystal is often conducted first to check the spread of the reciprocal space map and to judge the incident and receiving resolution. The reciprocal space map is then

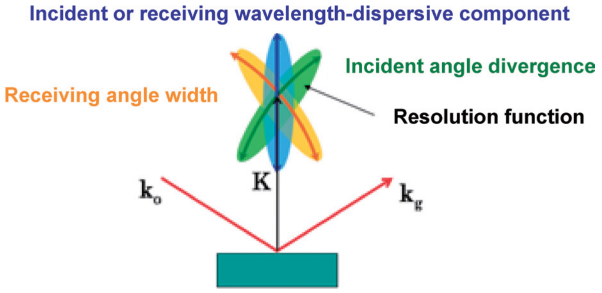
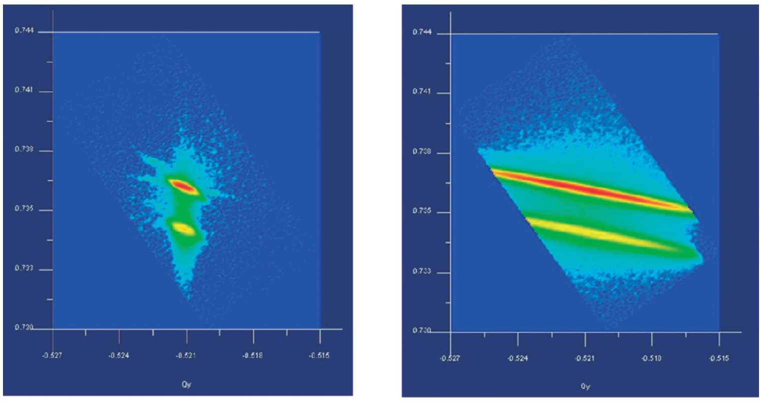


Fig. 20. Reciprocal lattice points and optical resolution.



High 2θ resolution **Low 2θ resolution**

Fig. 21. Comparison between high and low resolution reciprocal space map.

measured using an analyzer crystal if needed. To accurately measure the change in the position or spread of the reciprocal lattice point due to a change in crystal structure or degradation in crystallinity, a resolution function, which is sufficiently high relative to this change or spread, must be used. The optics for various measurements can be determined from the relationship between the size of the reciprocal lattice point to be measured and the resolution function of the measurement. Two examples of reciprocal space mapping data with different resolution in the receiving side are shown in Fig. 21.

For the case of low 2θ resolution, the reciprocal lattice point is spread as shown in Fig. 21. In this case, the analysis is difficult because the exact position of lattice point is very hard, if not impossible, to obtain. When measuring a reciprocal space map, it is necessary to pay attention not only to the incident optical system but also the receiving optical system. In the case of using a slit or a PSA (Parallel Slit Analyzer) for the receiving optics, the 2θ resolution is about 0.1 degree to 0.5 degree. In the case of using a crystal analyzer, the 2θ resolution is about 0.01 degree. However, the intensities obtained by using a crystal analyzer are one order of magnitude weaker than those of using a slit. So, it is preferable to use suitable optics to achieve a required resolution.

5. Concluding remarks

In this article, the methods for rocking curve measurement and reciprocal space mapping measurement have been described. One may get the impression that high-resolution diffractometry is difficult to measure and interpret. However, the recent advances in application software make it easy to perform high-resolution measurements and analyses. I would also think that the in-plane and the X-ray reflectivity methods should also be used to obtain more information on a sample. These techniques will be described in articles in the series of "X-ray thin-film measurement techniques" to appear in future issues of this journal.

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