

Real-time analysis and display function using SmartLab Studio II

Takahiro Kuzumaki and Aya Ogi*

1. Introduction

X-ray diffractometry is widely used in R&D and quality control to investigate the crystal structure of materials. It has a diverse range of application, and is used not only for qualitative and quantitative analysis of powder samples, but also to evaluate the aggregate structure of metal materials, analyze the crystal orientation of thin-film samples, and so forth. Previously, individual analysis programs were developed for each measurement and evaluation technique. Multiple applications had to be launched to finish evaluation, and the operation process could be complicated.

The integrated X-ray diffraction software suite SmartLab Studio II solves this problem by combining measurement and analysis functions into a single program. These functions are built on a common platform, which enables consistent and easy execution of tasks such as data display, data transfer when starting analysis, and creation of reports of analysis results^{(1), (2)}. Also, software startup time and the number of logins are minimized, and thus the workflow for the user is greatly improved.

Furthermore, SmartLab Studio II ver. 4 adds a real-time analysis function for simultaneously performing qualitative and quantitative analysis during measurement, and a real-time display function for pole figure and reciprocal space mapping measurement. The following provides details on real-time analysis, and presents examples of measurement.

2. Qualitative and quantitative analysis using the real-time analysis function

X-ray diffractometry is a technique for elucidating the crystal structure of a material using the diffracted X-rays produced when X-rays are irradiated onto a material in which atoms or molecules form a periodic array in three dimensions (i.e., a crystal). The peak positions and intensity ratios between diffraction peaks in a diffraction pattern vary depending on the crystal structure of the sample. The diffraction pattern is specific to the crystal phase, and thus qualitative analysis can be performed by comparing the diffraction patterns of known substances against the tested sample.

In addition, with X-ray diffractometry, simple quantitative analysis can be carried out using the integrated intensity of the strongest line and a reference

intensity ratio registered in a database. This analysis method is called the RIR method⁽³⁾.

The real-time analysis newly incorporated into SmartLab Studio II is a function for automatically performing qualitative analysis and quantitative analysis using the RIR method during measurement. Figure 1 shows a software screen from an XRD measurement for a mixture of three powder materials: corundum (α -Al₂O₃), rutile (TiO₂), and anatase (TiO₂). Each time the software automatically detects another diffraction peak, qualitative analysis is performed in real-time.

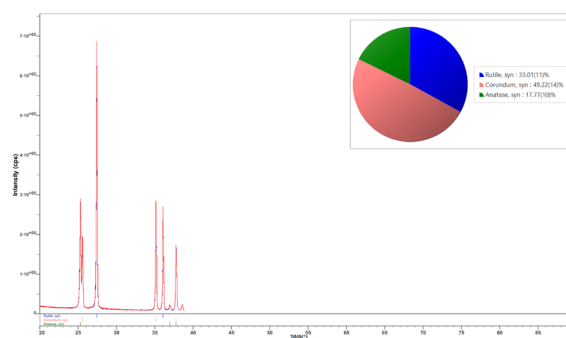


Fig. 1. Example of measurement using real-time analysis results.

In addition, if two or more crystal phases are identified, quantitative analysis is automatically performed using the RIR method, and the weight ratio of each crystal phase is calculated. Figure 1 demonstrates the preliminary results of quantitative analysis in a measurement that has only progressed to $2\theta=40^\circ$. The final result of quantitative analysis matched well with the mixing ratio of the prepared sample, as indicated in Table 1.

Because qualitative and quantitative analyses are performed while diffraction peaks are being observed, it

Table 1. Results of quantitative analysis of a mixed powder sample using the RIR method.

Crystal phase	mass%	
	Analysis value	Preparation value
Corundum (α -Al ₂ O ₃)	54.15 (18)	52.91
Rutile (TiO ₂)	33.71 (18)	34.22
Anatase (TiO ₂)	13.15 (8)	12.88

Figures in parentheses indicates standard deviations, e.g., 54.15 (18) indicates 54.15 ± 0.18 .

* Application Laboratories, Rigaku Corporation.

is possible to quickly check the crystal phases contained in a sample.

The powder XRD plugin is used to perform more detailed analysis; e.g., calculation of crystallite size or lattice constant refinement. Now, the desired analysis can be performed smoothly; measurement data is read into the Powder XRD plugin with a one-click operation and the results of real-time analysis can be saved together with the measurement data so that there is no need to perform qualitative analysis again.

3. Pole measurement using the real-time display function

The characteristics of polycrystalline materials, such as metals and polymers, are largely affected by the state of the aggregate structure, such as deviations of crystal orientation and crystal orientation distribution. Crystal orientation conditions can be estimated with an ω profile, a β profile, or a 2D diffraction image, but these techniques only evaluate the crystal orientation distribution within a narrow range. On the other hand, with pole figure measurements it is possible to acquire the crystal orientation distribution over a wide range by rotating the sample in all directions and observing the diffraction intensity. Various types of information concerning aggregate structure are revealed by a pole figure, such as crystal orientation and the degree of preferred orientation. Therefore, pole figure measurements are an extremely effective way to evaluate aggregate structure.

A pole figure measurement is performed by fixing 2θ at the diffraction angle of interest, varying two parameters— α (tilt angle of the sample) and β (in-plane rotation angle of the sample)—so that the sample is irradiated with X-rays from various directions, thereby investigating the α and β positions where strong diffraction X-rays are observed⁽⁴⁾. In pole figure measurements with a 0D detector, β is usually scanned while α is kept fixed (left side, Fig. 2). Measurement results are displayed as a pole figure. If the diffraction intensity at a certain α and β position is higher than in other regions, it means that the lattice planes of interest prefers to face in that direction.

In general, pole figure measurements take a long time; when a 0D detector is used, it requires a few hours or

more. Even if a 2D diffraction image is used, it takes a few tens of minutes. Also, it is difficult to infer the pole figure from measurement data (β profiles). When using conventional, individual software packages, it was not possible to ascertain the details of the pole figure unless the pole figure measurement was completed.

The real-time display function incorporated into SmartLab Studio II plots the diffraction intensity directly on a stereographic coordinate to show the measurement result as a pole figure. Figure 3 shows the measurement data (β profiles) and displayed pole figure in real-time of Cu (111) for a rolled copper plate, obtained using a 0D detector.

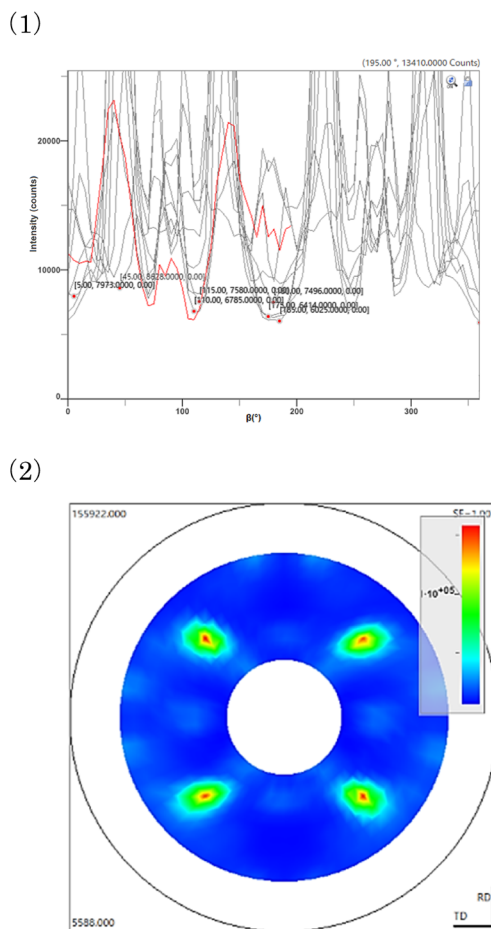
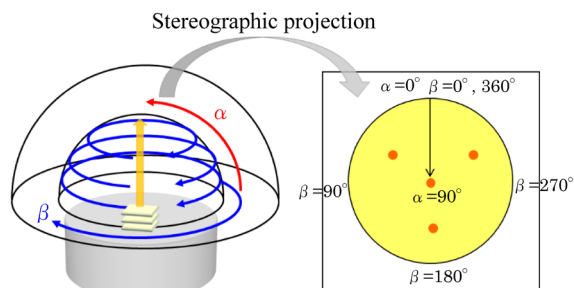


Fig. 3. Pole figure measurement observed with a 0D detector. (1) β profile, (2) the displayed pole figure using the real-time display function.



* $\alpha = 0^\circ$ and 90° may be reversed depending on definitions.

Fig. 2. Schematic diagram of pole figure measurement (left) and a pole figure (right).

With the real time display function, measurement data is added to the pole figure each time a β scan ends for a certain α angle. Therefore, it is possible to ascertain the crystal orientation distribution of the sample during the measurement.

With this sample, four strong peaks were observed at $\alpha = 35^\circ$ and $\beta = 45^\circ, 135^\circ, 225^\circ,$ and 315° . Based on a comparison with the standard stereographic projection of a cubic crystal, it demonstrated that the sample has a (111)[100] crystal orientation while measurement was in progress.

Using the Texture plugin, it is possible to perform detailed evaluation, such as volume percentage calculation of multiple preferred orientation components based on crystal orientation distribution (ODF) analysis.

4. Reciprocal space map measurement using the real-time display and analysis function

The characteristics of thin-film devices are determined not only by the chemical composition and crystal phases of their constituent materials, but also by their crystal orientation, crystallinity, and strain relaxation state. Reciprocal space mapping measurement, a technique for plotting the intensity of X-ray diffraction signals from a sample in reciprocal space, allows independent evaluation of the lattice spacing and crystal orientation distribution, and is appropriate for analysis of epitaxial thin films, as well as other thin-film samples.

A reciprocal space map is composed of multiple-scan data sets with varying combinations of the scattering angle (2θ) and the incident angle of X-rays to the sample (ω). Various measurement ranges, resolutions, and times required for measurement are available by selecting the optical devices used and the scan axes. SmartLab Studio II ver. 4 provides high-speed reciprocal space mapping measurements by combining a continuous scan with the omega-axis and 1D mode data collection using a multi-dimensional detector⁽⁵⁾. It allows a reciprocal space mapping measurement to be completed in an extremely short time—a few tens of seconds to a few minutes.

A reciprocal space map is analyzed by comparing measurement data with a simulation based on a film structure model. With the new function in SmartLab Studio II, measurement data can be plotted on reciprocal space coordinates during measurement, and a simulation can be overlaid on an observed reciprocal space map. This function makes it possible to examine the film structure model during measurement. Figure 4 shows the status of a high-speed reciprocal space mapping measurement of a GaN (15.2 nm)/Al_{0.08}Ga_{0.92}N (3.5 nm) multiple quantum well structure (5 periods) on a sapphire substrate, recorded in just 30 seconds. In a high-speed reciprocal space mapping measurement, 2θ angle vs. intensity data is output in seconds, and those data are plotted in real-time on the reciprocal space coordinates.

By inputting sample information such as crystal phase, crystal growth orientation, and composition ratio of each layer to the RS Viewer (reciprocal space map simulation), the positions of the calculated reciprocal lattice points are displayed overlaid on the reciprocal space map being measured. Using this function, it is possible to examine the validity of the predicted crystal phases or sample parameters while measurement is in progress. With this sample, it was confirmed that the observed reciprocal lattice points match with 0th-order reflection of the sapphire substrate and GaN. Satellite peaks attributable to the multiple quantum well structure were also observed.

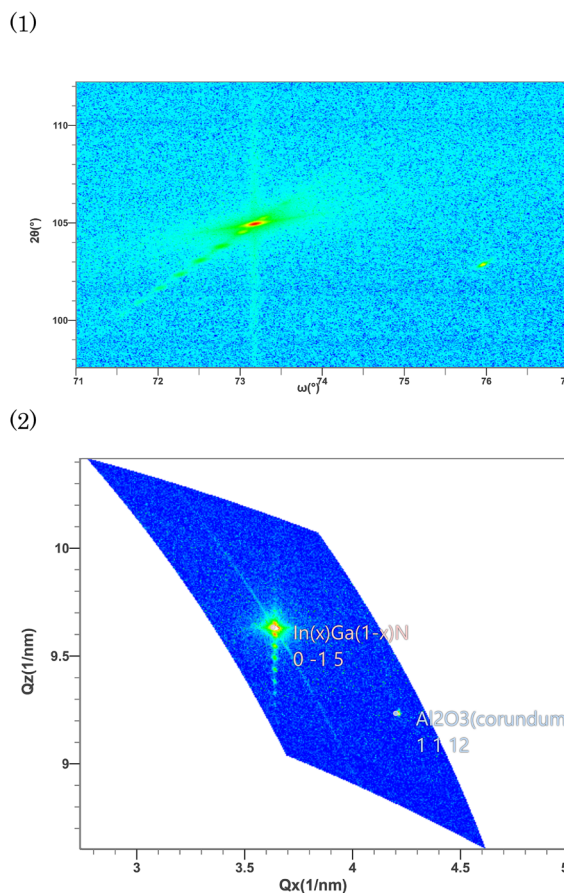


Fig. 4. Real-time analysis of high-speed reciprocal space mapping data for GaN/InGaN superlattice on a sapphire substrate.

- (1) 2D display of measurement data.
- (2) Real-time display of the reciprocal space map overlaid with a reciprocal lattice simulation.

The HRXRD plugin is used to perform more detailed analysis, e.g., calculation of the lattice constant in the out-of-plane or in-plane direction by indexing the coordinates of reciprocal lattice points, or evaluation of the crystal orientation distribution based on the cross-sectional profile of a reciprocal space map. A measured reciprocal space map is loaded into the HRXRD plugin through a one-click operation. The film structure already input to the RS Viewer can also be imported to the HRXRD plugin, and thus it is possible to start analysis smoothly without inputting the initial values for analysis again.

5. Conclusion

In this article, the new real-time analysis function of SmartLab Studio II was introduced with application examples. With this function, it is possible to perform easy qualitative and quantitative analysis of samples during measurement using profile measurement for powder samples. In addition, it allows users to display and check pole figure and reciprocal space map data, both of which require long times for measurement, while the measurement is in progress, and to smoothly

start advanced analysis. It is expected that this real-time analysis function will contribute to improving the efficiency of work that requires quick decisions, such as R&D and quality control.

References

- (1) *Rigaku Journal (English version)*, **31** (2015), No. 2, 25–26.
- (2) *Rigaku Journal (English version)*, **33** (2017), No. 2, 29–31.
- (3) C. R. Hubbard and R. L. Snyder: *Powder Diffr.*, (1988), **3**, 74.
- (4) K. Nagao and E. Kagami: *Rigaku Journal (English version)*, **27** (2011), No.2, 6–14.
- (5) S. Kobayashi and K. Inaba: *Rigaku Journal (English version)*, **28** (2012), No.1, 8–13.