X-ray thin-film measurement techniques

VI. Small Angle X-ray Scattering

Aya Ogi* and Katsuhiko Inaba*

1. Introduction

We have been making a series of papers for thin-film analysis techniques for characterization of crystalline qualities and crystal structures using High Resolution XRD (HR-XRD), or characterization of layer structures, such as film thickness, etc., using X-ray reflectivity (XRR) method. An X-ray analytical technique for the evaluation of particle/pore sizes will be explained in this paper.

Small Angle X-ray Scattering (SAXS) technique is a technique mostly used for characterization of the size distributions of particle sizes dispersed in liquid medium, or those of pores/textures in porous bulk samples. Due to the sample configuration, the analysis is used to be performed using transmission geometry through sample bodies. However, in applying this technique to thin film samples, a reflection geometry is required since the absorption due to thick substrates is the great obstacle to detect the weakly scattered signals from thin films or their surfaces. This situation is inevitable since nano- or sub-micron scaled surface textures or structures formed on sample surfaces are the main target of this analysis.

In this paper, a general feature of SAXS measurement and analysis with the transmission geometry will be briefly mentioned first. Then, details of SAXS measurement/analysis technique in transmission geometry applied for thin film samples will be shown together with the applications to the functional thin film samples.

2. What is SAXS?

It is convenient to start with the definition of SAXS analysis method. SAXS analysis is a method to analyze the "size distribution" of particles or pores of nanometer size dispersed within samples. Features of this method are as follows[1],[2];

1. It is possible to evaluate particle/pore size distributions of amorphous materials, as well as crystalline materials, though the model analysis of density fluctuation in materials.
2. It is possible to evaluate particle/pore size distributions of a sample in non-destructive way and in a short time.
3. It is possible to characterize non-transparent samples with visible light.
4. Sizes possible to analyze are from 1 nm to ca. 100 nm.
5. It is possible to evaluate the averaged size with the assumption of the shapes of particles/pores.
6. It is possible to analyze the sizes of particles with complex structures like core-shell structure.

A comparison with other techniques for the particle size evaluation is summarized in Table 1.

2.1. Scattering phenomena and the technical issues in SAXS

Let us imagine a sample with a density fluctuation of nanometer-size within its body (commonly called as host matrix), as simply illustrated like colloids with particles in dispersion medium. The Incident X-ray is scattered by particles with a small scattering angle 2θ, in the region close to zero, as shown in Fig. 1.

Sizes (and size distribution), shapes of particles, or correlated length between particles can be analyzed from SAXS profiles, where scattered signals are shown as a function of scattering angle. As can be seen from Fig. 1, the accessible smallest 2θ position is defined by the beam size of the direct beam, so that the collimated parallel beam should be employed for the incident beam, at least in the vertical direction in the Fig. 1. And also, it is better to suppress signals from matrices as possible, for the analysis. If this situation is not attainable, it would be better for analysis to employ a measure data with a sample without particles as a reference blank data. Additionally, the thickness of samples or the concentration of particles should be adjusted for the data acquisition of better quality.

Figure 2 shows an image of the dimension of scattering body analyzed with SAXS. Like the case of crystallite analysis[3] in XRD, one-dimensional size of scatters (particles) along the scattering vector can be analyzed in SAXS. If the anisotropy of size distribution in sample is expected, the sample should be properly positioned to direct its orientation to the scattering vector.

Size distribution can be also analyzed by modeling scatters' shape and their size distribution, by fitting the calculated intensity profiles to the observed profiles. Details are shown in Reference (1).

* X-ray Research Laboratory, Rigaku Corporation.

Table 1. A comparison between analysis methods for particle size distribution evaluation.

Method	Advantages	Disadvantages
Transmission Electron Microscopy	The real images (shapes) of the particles are observed.	It is difficult to estimate the average structure.
Dynamic Light Scattering	The wide range of particle size (1 nm~6 μm) can be evaluated.	Concentration and measurement temperature affect the result.
Laser scattering particle size analysis	The wide range of particle size (15 nm~500 μm) can be evaluated.	The particles have to be dispersed in a solvent.
Differential Mobility Analysis	Not only size distribution analysis but also size classification is available.	Particles captured in matrices are not detected.
Time-of-Flight Second Ion Mass Spectrometry	The number of atoms composing a particle is obtained.	The range of particle size detected is limited to up to several nm.
Small Angle X-ray Scattering	Any forms of samples can be analyzed non-destructively.	The model of scatters' shape is required in the calculation process.

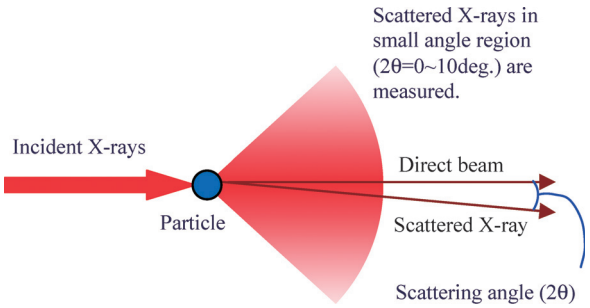

Fig. 1. The schematic of SAXS.

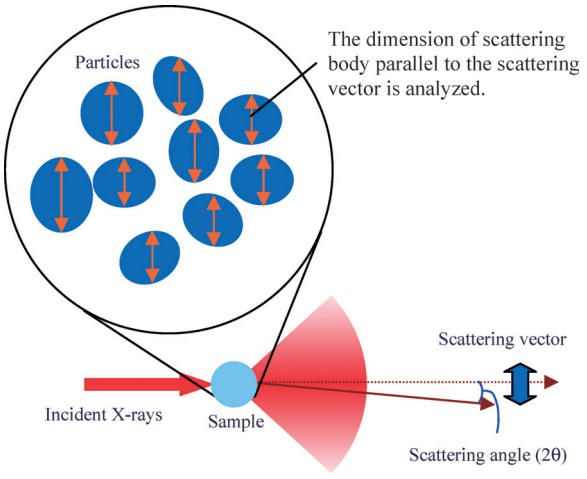

Fig. 2. The particle size analyzed from SAXS measurement.

2.2. SAXS with Thin Films—a reflection geometry—

In case where the targets for the SAXS analysis are thin films grown on substrates, or their surface textures over them, a reflection geometry is commonly employed in SAXS measurement. In this geometry, a preliminary preparation of sample thickness to set an adequate absorption is no more required. Instead, weak signals should be effectively collected, due to the small sample volume (thickness) or in order to analyze the surface structures fabricated naturally or artificially[4]. This issue

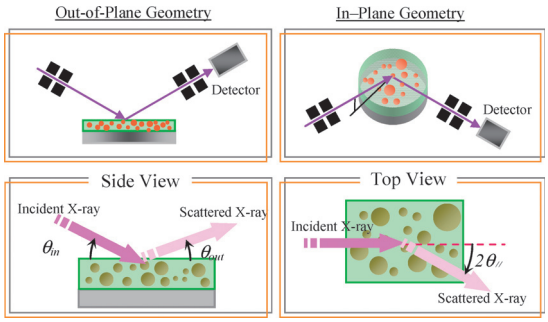

Fig. 3. Two geometries of GI-SAXS.

is analogously discussed with the "out-of-plane XRD" technique[5] and "in-plane XRD" technique[6]. For this purpose, the incident X-ray should hit on sample surface with a Grazing-Incidence geometry at the incident angle close to the total external reflection, so that this SAXS method is used to be called as Grazing-Incidence Small-Angle X-ray Scattering method, and is abbreviated as GI-SAXS[4].

Two geometries analogous to the asymmetric-reflection XRD measurement and in-plane XRD measurement are possible in GI-SAXS, as shown in Fig. 3.

Physical parameters of films, such as film thickness, its density, its surface roughness or its interface roughness between the substrate, are indispensable for the precise GI-SAXS analysis. So the X-ray Reflectivity (XRR) measurement and analysis[7] should be performed prior to the SAXS analysis.

Precise GI-SAXS analysis should take into account the reflection and scattering at the interfaces between film and substrate. Details of GI-SAXS analysis method is well described in the Ref. (4) and (8)–(10).

2.2.1. GI-SAXS—out-of-plane geometry—

The out-of-plane GI-SAXS geometry is shown in the left side column of Fig. 3. In case where the θ_{in} (incident angle) is equal to θ_{out} (exit angle), a specular reflection is detected in the measurement, thus, this is XRR

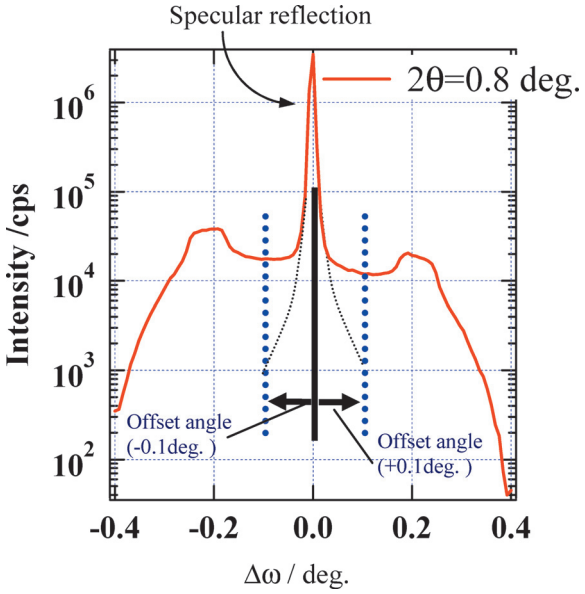

Fig 4. An example of rocking scan observed with fixing 2θ axis (0.8 deg.).

measurement (an optical system employed is also the same). This indicates that both of the specular reflection and the SAXS are detected in this geometry. However, the intensity due to the latter is generally extremely small, so that the SAXS signals are screened with the huge signals by specular reflection.

In order to record the SAXS signal effectively, in other word, to escape from the specular reflection, so-called "offset scan" is convenient for SAXS measurement[8)-(10)]. The offset scan is performed by the motion of $2\theta/\omega$ scan in the condition where the equality of θ_{in} and θ_{out} is intentionally broken. The appropriate shifting parameter ($\Delta\omega$) of ω (incident angle) from the half of 2θ can be determined from the analysis of rocking curve profile for specular reflection. An example is shown in Fig. 4. The profile shown in Fig. 4 is a ω scan rocking curve at 2θ=0.8 deg. The horizontal axis is shown with $\Delta\omega$ (shift of ω from the half of 2θ), and thus $\Delta\omega$=0 corresponds to condition where the specular reflection is detected.

Two blue dotted lines indicate the position of $\Delta\omega$ of +/− 0.1 deg, where the specular reflection signals are greatly reduced (envelopes are shown in small dotted lines). Though the $\Delta\omega$ can be set as either −0.1 deg. or +0.1 deg., the contribution of surface roughness should be enhanced in the geometry of $\Delta\omega$=−0.1 deg. It is recommended to perform these ω-scan rocking curves at the 2θ position of 0.5 deg. to 1.0 deg. to check the contribution of specular reflection.

Some application results will be shown for SAXS analyses using the offset scan data[8)-(10)]. Samples are the organic low-k dielectric films with porous structures, fabricated on Si substrates. The diameter of pores is considered as the crucial factor for the rigidity of framework of the film sustaining Cu interconnecting layers grown on it. The thickness of low-k films are confirmed as 400 nm from the XRR analysis. Three

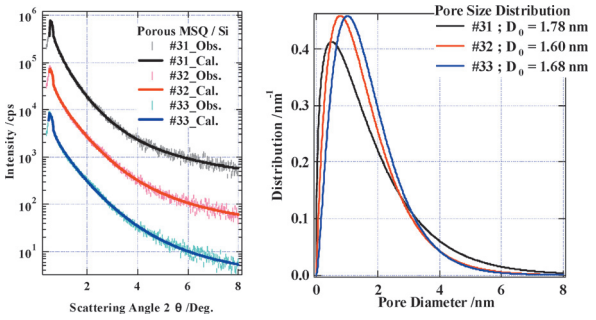

Fig 5. Left: SAXS profiles observed. Right: The results of size distribution analysis.

samples with different fabrication processes were analyzed. SAXS profiles for these three samples are shown in the left side of Fig. 5, and the analytical results for their size distribution of nanometer-sized pores are shown in the right side of Fig. 5.

The difference of the fabrication process is found to cause the different size distribution of pores. The pore size distribution determined with other techniques like the N_2 gas adsorption technique and the positron annihilation lifetime spectroscopy showed the same results obtained from SAXS analysis, indicating the validity of the SAXS analysis.

2.2.2. GI-SAXS—in-plane geometry—

The in-plane GI-SAXS geometry is shown in the right side column of Fig. 3. With this geometry, the huge specular reflection does no more overlap to the SAXS signals since the detector moves to the direction perpendicular to the specular reflection. So, the offset scan is not required in this geometry. Instead, the foot print of the incident X-ray projected on sample surface should be taken into account, as is the same with "in-plane XRD" measurements.

The collimation of the incident X-ray should be severely maintained as discussed in section 2.1. This collimation is sufficient only in the vertical direction (along the surface normal direction) in the left figure of Fig. 3 for the out-of-plane geometry. However, the additional collimation along the surface plane (the vertical direction in the right figure in Fig. 3) is required for in-plane geometry. It is possible to employ the Parallel Slit Collimator (PSC) for this collimation as explained in the paper for in-plane XRD technique[6)]. However, the collimation with this tool is not sufficient for GI-SAXS of in-plane geometry in most cases. Another candidate is the confocal-type double parabolic multilayered mirror optics[4),(10)], using a point focus X-ray source. The brilliance and the collimation with this optics are far superior to the pin-hole optics.

The analytical result for Ni granular nano-particles in carbon matrix is shown as an application example for the GI-SAXS with the in-plane geometry[12)]. This material is a possible candidate for the high-density magnetic recording medium in future.

The analytical results for the size (diameter) distributions of this sample containing Ni granular particles are shown in Fig. 6, where the dashed line

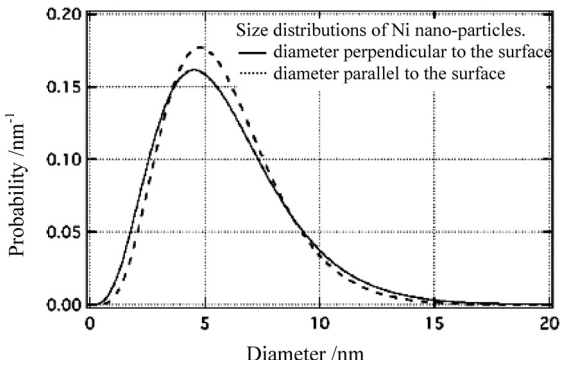

Fig 6. Size distributions of Ni nano particle.

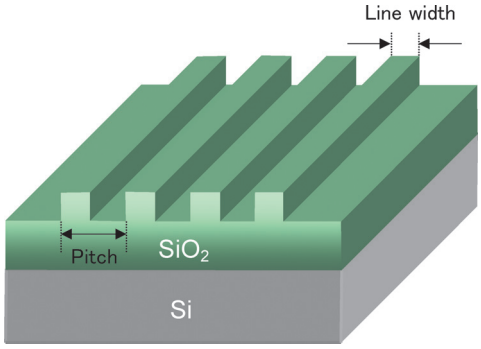

Fig 7. The schematic of a submicron-scale grooves on sample surface.

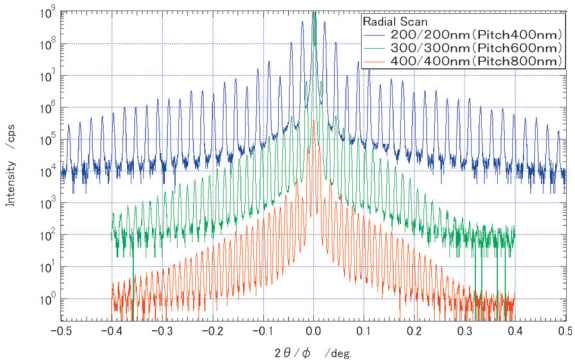

Fig 8. High-resolution GI-SAXS profiles of micro structure surfaces.

shows a result analyzed from the profile from GI-SAXS with the in-plane geometry, *i.e.* the size along the sample surface. Instead, the solid line shows a result analyzed from the profile from an offset scan in GI-SAXS with the out-of-plane geometry, *i.e.* the size along the surface normal direction.

From these results, it can be concluded that the Ni granular nano-particles exhibit an isotropic size and size distribution with the averaged diameter of approx. 5 nm. These results are consistent with the analysis with the Transmission Electron Microscopy (TEM), though the latter technique is a destructive one.

A further investigation using XRD reveals a very interesting fact. The crystallite sizes along both parallel/normal to sample surface are also evaluated using out-of-plane and in-plane XRD techniques, respectively. The crystallite sizes along both directions are evaluated as 5 nm. The crystallite size obtained from XRD analysis is identical with the particle size obtained from GI-SAXS analysis, implying that each Ni nano-particle is in the single crystalline nature. Combining the data analysis from XRD and GI-SAXS, it is concluded that the present sample containing Ni granular particles dispersed in carbon matrix are isotropic size (5 nm in diameter) and size distribution, and each of Ni particles is expected to be a single crystalline grain.

3. Advanced Analysis with GI-SAXS

In this section, a cutting-edge analysis method with GI-SAXS is introduced, which will play as a powerful and useful tool for the analysis of the functional devices in future.

3.1. Profiling of surface periodic structures[4],[13]

Periodic surface structures composed of lines and spaces are frequently formed during the fabrication process of electronic, optical, or magnetic devices: semiconductor memories, semiconductor lasers, magnetic recording devices being cases in point. Characterization of such structures in terms of line-widths, pitches, and height/depth is very important for precise control of the fabrication process. The analysis using GI-SAXS is of great interest as an indispensable tool for the characterization of nanometer-scaled surface periodic structures. The Atomic Force Microscopy (AFM) and Scanning probe Electron Microscopy (SEM) are also employed for the characterization of surface periodic structures, directly revealing the size or shape of each constituent unit of periodic structure. The GI-SAXS analysis is employed complementarily with AFM or SEM characterization, since the averaged size over a wide range on surfaces or the size distribution can be analyzed from GI-SAXS analysis.

The analytical result for the surface grating structure is shown in this section.

The sample has the surface periodic grooves of sub-micron scale formed on thermally oxidized Si substrate using Electron Beam (EB) lithography method, as schematically shown in Fig. 7. The depth of grooves was approx. 10 nm, evaluated from the XRR analysis.

The GI-SAXS analyses were performed on three samples with different periodicities (pitches), such as 400, 600, 800 nm. Such a long period requires a high resolution in receiving optics in measurements, thus, a channel-cut analyzer optics for SAXS measurement was employed[13]. The GI-SAXS profiles obtained are shown in Fig. 8. The precise analysis of the positions of peaks and their orders reveals that the average periodicity was determined with an extremely low uncertainty of less than 0.02%.

As a next step of analysis, a diversity of cross-sectional profile of groove lines from a rectangular shape was taken into account. The calculation of scattered intensity was performed by fitting a newly introduced

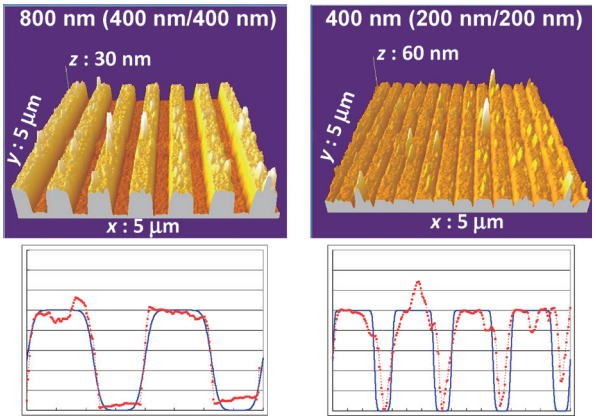

Fig 9. Upper: AFM images of submicron-scale grooves with 800 nm pitch (left) and 400 nm pitch (right).
Lower: The comparison of the results of profile analysis between GI-SAXS (blue solid line) and AFM (red broken line).

· parameter and model as below.
· ratio of the width of line to that of space
· a trapezoidal shape with round corners is assumed for the cross-sectional profile for every line of periodic patterns

Results are shown in Fig. 9, together with results from AFM observation. Upper two figures in Fig.9 are the AFM images for 800 nm pitch and 400 nm pitch samples. Lower two figures in Fig. 9 are the cross-sectional profiles analyzed from GI-SAXS (blue solid lines) and from AFM (red broken lines). GI-SAXS and AFM analysis show a good coincidence with each other. In a smaller pitch sample (400nm), it can be found that the EB lithography did not sufficiently etch grooves, so that the ratio of the width of line to that of space is deviated from 1:1, but close to 7 : 3.

In recent researches for material science or device technology, GI-SAXS technique comes to be an indispensable analysis tool for surface nano-structures in the field of semiconductor or magnetic applications etc[14]–[18].

3.2. Employment of 2-dimensional detector

Though the spatial (angular) resolution is limited, the employment of 2-dimensional (2D) detector for GI-SAXS measurement is useful, with the combination of point-focused incident optics[4]. While the 2D detector can cover a relatively wide range of scattering angle in directions both of normal/parallel to sample surface, long and wide range of scanning is required with the use of a conventional 0-dimenstional detector. The combination of a point-focused optics and 2D detector system in GI-SAXS analysis will be a splendid tool for the investigation of samples exhibiting fast reaction with varying temperature and/or time[19].

4. Conclusion

This paper has focused on the SAXS technique applied for thin film samples. Because of the sample dimension and configuration, GI-SAXS of a reflection geometry is generally employed for thin film samples. The combination of GI-SAXS with XRR analysis will lead to a thorough analysis of layer structures, while the combination with XRD analysis will help us to have a crystallographically clear image of materials.

Geometrical characterization of structures built on the surface of materials has become increasingly important. GI-SAXS technique must play an irreplaceable role with other techniques for the characterization of thin film surfaces.

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