

Maximum Smoothness Method for Nondestructive XPS Depth Analysis

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Analysis of the structure and composition of materials is essential for product development and quality improvement. The objects of analysis may include semiconductor substrates, plating, and resin surface finishes, specifically the depth profile of chemical species near the surface, and many other determinants of product characteristics. Nondestructive evaluation of depth profiles for individual chemical species in unknown samples is difficult with existing analytical methods. Thus, to meet this need, we have developed a new data analysis technique for angle-resolved X-ray photoelectron spectroscopy (ARXPS), dubbed the maximum smoothness method (MSM). In combination with obtaining depth information using the three XPS systems available to our company, MSM analysis enables nondestructive evaluation of profiles at wide depth ranges. Here, we describe MSM analysis using the three XPS systems and nondestructive depth profile evaluation for a wide range of products.

Keywords: angle-resolved X-ray photoelectron spectroscopy (ARXPS), nondestructive, depth profile, convex quadratic programming problem

1. Introduction

For product development and quality improvement, analysis of the structure and composition of materials is essential in fields such as semiconductor substrates, platings, resin surface finishes, and many others in which the state of the surface region affects the product characteristics. The product evaluation requires determining the depth profiles of chemical species from the surface to depths of several tens of nanometers.

The methods for nanometer-order depth profile evaluation can be broadly categorized as shown in Fig. 1. Category A, consisting of excision of an evaluation region from the sample and analyzing its cross section, includes the main techniques such as cross-sectional scanning transmission electron microscopy (STEM)*¹ and energy-dispersive X-ray spectroscopy (EDX)*². Category B involves repeated alternation between ion sputtering and surface analysis, and is represented by X-ray photoelectron spectroscopy (XPS)*³ which is the main technique considered in the present study.

Categories A and B in Fig. 1 are standard analysis techniques that provide high reliability. However, both require sample destruction which may alter the state of the sample. We therefore focus on Category C, nondestructive

analysis, shown in Fig. 1, which involves nondestructive surface analysis together with derivation of the depth profile by mathematical analysis of the obtained measurement data. In this paper, we report the principles and applications of a newly developed data analysis technique for nondestructive depth profile evaluation.

2. Nondestructive Depth Profile Evaluation Technique

2-1 Angle-resolved XPS analysis

Angle-resolved XPS (ARXPS) measurement data used for nondestructive depth profile evaluation, shown in Fig. 2, are obtained by modifying the photoelectron takeoff angle (relative angle between detector and sample; 90° and 15° examples are shown in Figs. 2 (A) and 2 (B), respectively) to change the information depth (yellow region in Fig. 2). More specifically, as in Fig. 2 (A), selective detection of photoelectron emission perpendicular to the sample

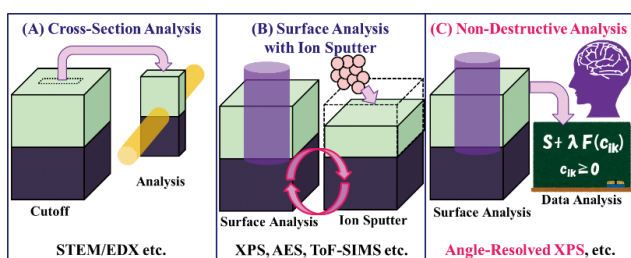


Fig. 1. Methods for depth profile evaluation

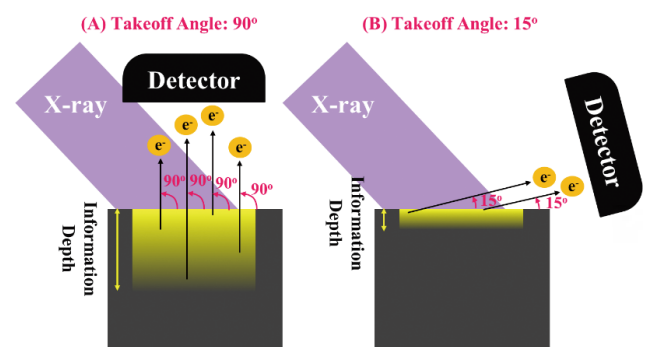


Fig. 2. Schematic of ARXPS analysis

surface will yield averaged information over a region extending relatively deep into the sample, whereas in Fig 2 (B), selective detection of photoelectrons emitted parallel to the sample surface will yield information for a relatively shallow region of the sample. ARXPS analysis of the XPS surface analysis data with multiple photoelectron takeoff angles will then provide an important perspective on the depth profile of chemicals.

However, the XPS data obtained at each takeoff angle represents the information of a region extending from the topmost surface to a specific level, rather than the information of individual depth segments within the measured region. This may pose some difficulty with regard to the mathematics needed to obtain the depth profile. The maximum entropy method⁴ has often been applied to such problems. Many cases of its application in various fields of research have been reported,⁽¹⁾⁻⁽⁷⁾ and now analytical laboratories have been providing commercial evaluation services based on this technique,^{(8),(9)} with excellent results for a wide range of materials. This method, however, generally requires the assumption of initial depth profiles. In many cases the structure of the material to be assessed is not clearly known. Therefore, no reliable initial profile can be assumed.

2-2 MSM data analysis technique

We therefore developed the “maximum smoothness method” (MSM) as an original ARXPS data analysis technique that can be applied to samples of unknown structure. Here, we describe the general concept of MSM in Fig. 3. The mathematical details are provided in a separate paper.^{(10),(11)} In the following discussion, indices i, j , and k correspond to the chemicals, the takeoff angles, and the depth, respectively.

The desired final depth profile (Fig. 3 (A)) is expressed as c_{ik} ($i:1\sim I, k:1\sim K$). The theoretical measurement values that should be obtained when a sample having that profile is analyzed by ARXPS are shown in Fig. 3 (C), and the overall system smoothness (Fig. 3 (E)) is a function that includes the variable c_{ik} . We will later describe the meaning of the equation that expresses the smoothness. The sum of smoothness (Fig. 3 (E)) and the squared deviations (Fig. 3 (D)) between the theoretical values (Fig. 3 (C)) and the experimentally obtained ARXPS data (Fig. 3 (B)) represent the function to be minimized. The term “maximum smoothness method” is associated with minimizing the quantity shown in Fig. 3 (E) (maximizing the smoothness) together with the sum of the squared deviations (Fig. 3 (D)).

Various means of expressing the smoothness of the depth profile can be considered, but for the MSM we have chosen the sum of squares of concentration variations with depth for each chemical species (Fig. 3 (E)), a quantity known as the Dirichlet energy^{*5} of the system.

Consider the dependence of the minimization target function (Fig. 3 (D)-(E)) on the relative concentration c_{ik} . Because the theoretical measurement value d_{ij} is proportional to the relative concentration (the relative concentration multiplied by its ionic cross section, which is a constant for each chemical species), the sum of the squared deviations between d_{ij} and the actual measurement data is proportional to the square of the relative concentration, as is the Dirichlet energy. Thus, the function to be minimized in the MSM is a quadratic function of the relative concen-

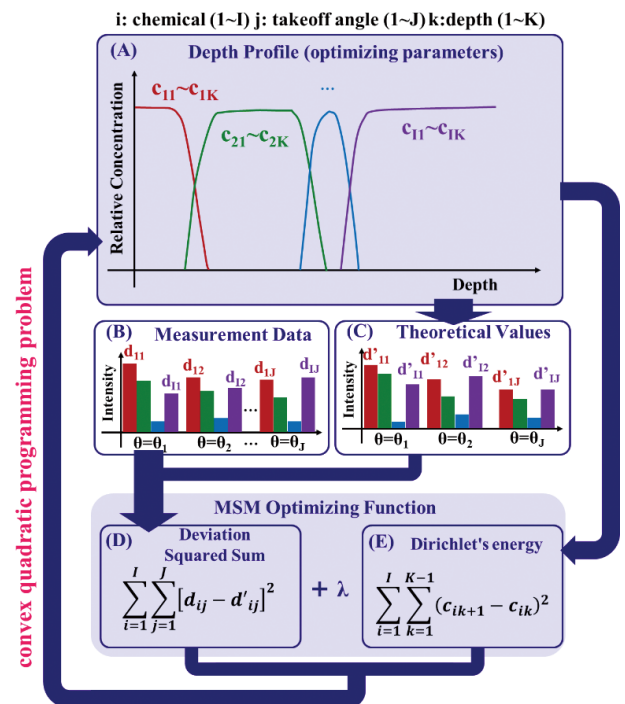


Fig. 3. MSM general concept

tration which is the parameter varied during the minimization process. In addition, it is not simply a quadratic function but rather a convex quadratic function^{*6} which is convenient for minimization.⁽¹⁰⁾

In nonlinear function minimization, the initial parameter value is first set and small changes are then repeatedly made. The result is known to depend on the initial value. In the maximum entropy method which uses a logarithmic function of the concentration as the entropy term, this challenge also exists. With the MSM, in contrast, the minimization target function is a convex quadratic function and its minimization is a convex quadratic programming problem^{*7} for which a global optimum solution can be rapidly obtained with the sophisticated algorithms such as active set method^{*8}.

With the MSM, which itself is a convex quadratic programming problem, it is unnecessary to utilize a series of calculations starting from an initial value such as that required for other nonlinear programming problems. The solution (depth profile) is output simply following input of the measurement data and necessary parameters. Thus, in the MSM analysis, unlike in the maximum entropy method, no preliminary profile assumption is necessary, and the depth profile can be derived simply from the measurement data alone. This is the main advantage of adopting the Dirichlet energy as the smoothness indicator.

In addition to the measurement data, if preliminary information for the samples (such as the ratios between the concentrations of certain chemical species obtained from sources such as literatures and other analyses) are available, they can be used to assign limiting to the solutions. The technique thus enables a flexible approach for obtaining solutions in accordance with the context and goal of the particular application.

3. MSM Analysis Examples

3-1 XPS systems in use by our company

The information depth of the XPS analysis can be changed by modifying the takeoff angle, as noted in Sec. 2-1, but it also changes with the applied X-ray energy. The information depth will generally be shallow for low-energy X-rays and deep for high-energy X-ray. Each of the three XPS systems available to our company can provide a different range of information depths (Table 1).

Table 1. XPS systems accessible to Sumitomo Electric and typical specifications

Facility	X-ray Source (eV)	Analysis depth
(A) SAGA-LS (BL17)	50-1500	< 1-3 nm
(B) Lab (Osaka)	1487 (Al K α)	< 10 nm
(C) SPring-8 (BL16XU)	6000-10000	< 30 nm

The Sumitomo Electric Beamline (experimental station) of the SAGA Light Source (SAGA-LS) in the Kyushu Synchrotron Light Research Center*⁹ is most appropriate for low-energy, ultra-shallow (< 3 nm) XPS analysis (Table 1 (A)).⁽¹²⁾ For the Lab XPS in our Osaka Works, the Al K α radiation source enables XPS analysis to depths of approximately 10 nm (Table 1 (B)). The SPring-8*¹⁰ world-class radiation light facility, which serves the Sunbeam Consortium of thirteen companies including our own, is home to the exclusive BL16XU beamline enabling high-energy deeper XPS (< 30 nm) analysis (Table 1 (C)).⁽¹³⁾

MSM analysis is widely applicable, regardless of the X-ray energy, and can be used in conjunction with any of these three XPS systems in accordance with the objectives. Here, we describe three example applications for each system. A simultaneous analysis of data from these three XPS systems has been demonstrated in a recent paper.⁽¹¹⁾

3-2 Example 1: Thin SiON film on Si, at Lab XPS⁽¹⁰⁾

We first describe the case of a sample having a SiON film formed on a Si substrate by chemical vapor deposition. This case is also discussed in detail in a separate paper.⁽¹⁰⁾ In this case, a cross-sectional STEM/EDX analysis was also performed for comparison with the MSM analysis results (Fig. 4). The results show that the SiN film is approximately 5 nm thick and that the SiON film composition is not constant in the depth direction, but consists of a 3-layer structure of Si oxide/Si nitride/Si oxide.

The results of the ARXPS analysis of this sample are shown in Fig. 5. The signals for single-crystal Si, O-bonded Si, and N-bonded Si are designated Si2p(Si), Si2p(SiO), and Si2p(SiN), respectively. The results of Fig. 5 suggests a structure consisting of a Si oxide film at the surface and a Si nitride film and Si substrate at a deeper level, but specific film thicknesses and other information could not be ascertained, making comparative discussion of the samples difficult.

The results of the MSM analysis using the data shown in Fig. 5 are presented in Fig. 6, with the single-crystal Si, O-bonded Si, and N-bonded Si designated as Si(Si), Si(SiO), and Si(SiN), respectively. They show that the SiON film has a 3-layer structure consisting of oxide,

nitride, and oxide, and that the total film thickness is approximately 5 nm, and thus matched the results of the cross-sectional STEM/EDX analysis shown in Fig. 4.

One of the biggest advantage of ARXPS/MSM is that it allows the chemical state to be determined. The three states of Si in this example are effectively differentiated as

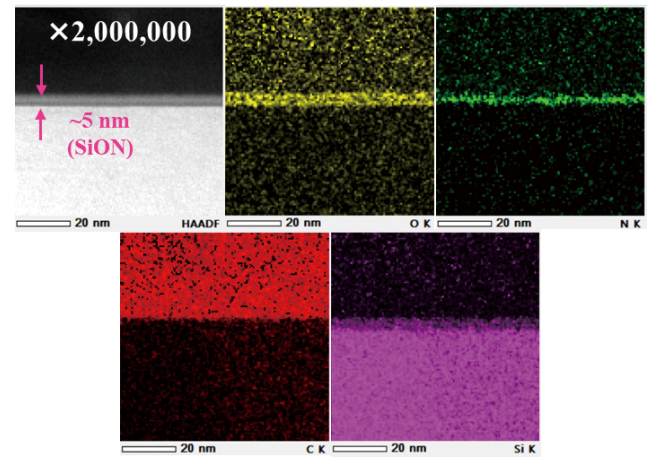


Fig. 4. Results of cross-sectional STEM/EDX analysis of sample with SiON film on Si

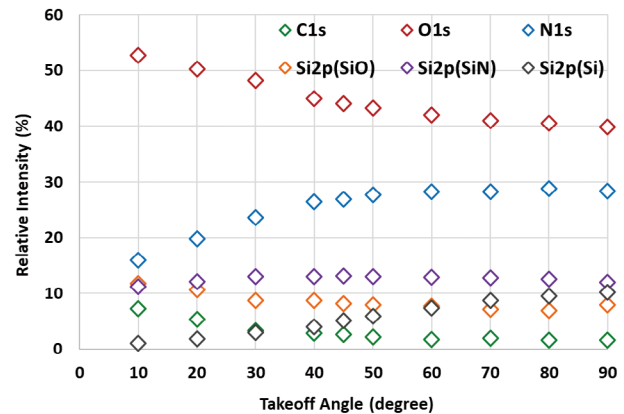


Fig. 5. Results of ARXPS analysis of sample with SiON film on Si

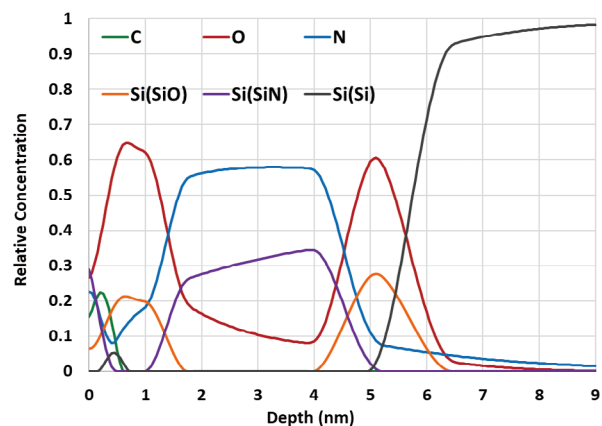


Fig. 6. Results of MSM analysis of sample

Si-bonded Si, O-bonded Si, and N-bonded Si. Such separate depth profiling for each chemical state, which is difficult to be achieved by methods such as those in Category A (cross-sectional STEM/EDX) or Category B (XPS with ion sputtering) shown in Fig. 1, represents a further major advantage of analysis by ARXPS/MSM.

3-3 Example 2: SiN film on InP, at SPring-8

The next example involved a SiN film with an estimated thickness of approximately 10 nm on an InP substrate. We therefore used the SPring-8 BL16XU (incident X-rays: 7,940 eV) capable of deeper-level analysis than the Lab XPS. To prevent electrostatic charging of the sample surface, the sample was coated with Au (approximately 5 nm thick) to give a sample structure of Au/SiN/InP.

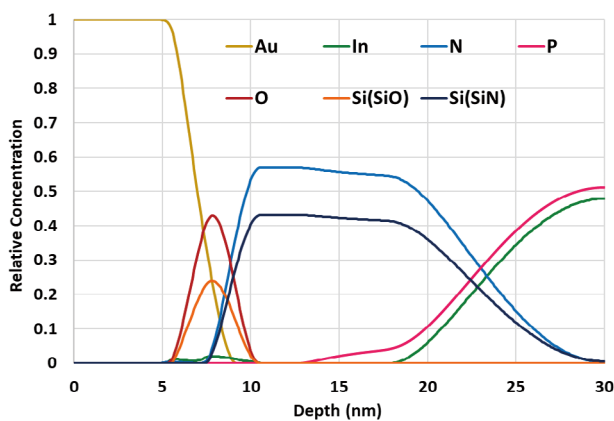


Fig. 7. Results of MSM analysis of sample with SiN on InP

The MSM analysis was performed with data from the ARXPS analysis at takeoff angles of 50° and 85°. As shown in Fig. 7, the Au/SiN/InP structure was correctly identified, in addition to a thin Si-oxide film on the SiN surface. Although the profile was somewhat unclear when obtained with only the two takeoff angle data, knowing in advance that the sample surface was Au allowed the range of possible solutions to be constrained, thus resulting in an accurate solution. This demonstrates an additional strength of MSM analysis: its amenability to free application of constraints appropriate to the analytical circumstances.

3-4 Example 3: GaN substrate, at SAGA-LS

In the third and final example, we evaluated the state of an oxide film (approximately 1 nm thick) on the surface of a GaN substrate, at BL17 (incident X-rays: 600 eV) of the Kyushu Synchrotron Light Research Center (SAGA-LS), which is appropriate for evaluation of shallow regions. Figure 8 shows the results of the MSM analysis using data obtained with takeoff angles of 30°, 45°, and 85°. The Ga-oxide film/GaN substrate structure is effectively identified. It is also possible to ascertain differences in the Ga-oxide film thickness and other information by similar evaluations of sample groups produced using differing processing conditions.

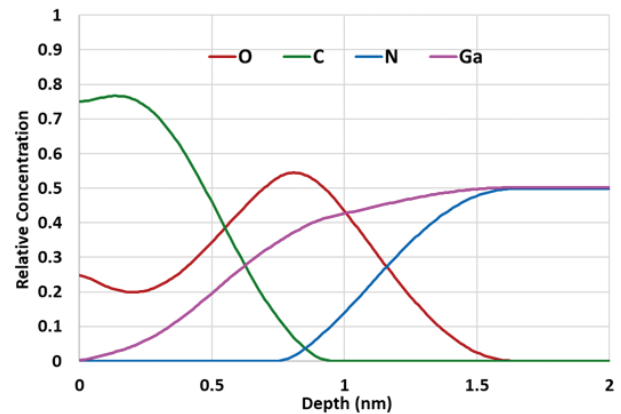


Fig. 8. Results of MSM analysis of GaN-substrate samples

4. Conclusion

We have developed an original angle-resolved XPS data analysis technique, maximum smoothness method (MSM), for non-destructive evaluation of sample surfaces. Its main advantages are that, unlike the existing maximum entropy method, it requires no initial values, and it can effectively be applied at the analysis site to assess samples with unknown structures and components.

Through utilization of this new technique in conjunction with our company's access to the three XPS systems, it has become possible to assess the depth profiles of surface regions of many types of samples. The appropriate combination with STEM/EDX and other existing analysis methods is expected to lead to determination of a broad range of phenomena and increased product quality.

5. Acknowledgements

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Technical Terms

- *1 STEM: Scanning transmission electron microscopy, a technique for obtaining images by detection of electrons penetrating a sample while scanning using a narrowly focused electron beam. One of the most famous method of nanometer-order observation of sample cross sections.
- *2 EDX: Energy dispersive X-ray spectroscopy, a widely used technique for elemental analysis to investigate and identify elements contained in samples based on their characteristic X-rays. A combination of EDX and STEM is often used in conjunction with MSM analysis.
- *3 XPS: X-ray photoelectron spectroscopy, a surface analysis technique and key subject of this paper. A method for analysis of elements and their chemical

states by irradiating samples with X-rays and detecting the emitted photoelectrons. From the measurement data, the average composition of the entire information depth range is commonly interpreted as the sample-surface composition. However, in the MSM analysis in the present study, the information is extracted for each depth rather than as an average for all measurement depths.

- *4 Maximum entropy method: One of the main techniques for estimating the state of a target based on low-quantity, noisy, or other such datasets. Based on the concept of “entropy is highest for systems in the natural world”. Although it has a proven track record in many fields, for ARXPS data analysis of some samples it is difficult to apply due to the requirement of initial values. We have now overcome this problem by the development of the MSM.
- *5 Dirichlet energy: A concept for determining how a function varies. Originally defined as the integral of the squares of the gradient of a function throughout its space. In MSM analysis, it corresponds to the sum of the squares of the variation in discrete relative concentrations.
- *6 Convex quadratic function: If a real-number function f defined for a certain range of variables for two arbitrary points \mathbf{u} , \mathbf{v} in the domain (both are variable sets) and an arbitrary real number meeting the condition $0 \leq \alpha \leq 1$ satisfies

$$f[(1-\alpha)\mathbf{u}+\alpha\mathbf{v}] \leq (1-\alpha)f(\mathbf{u}) + \alpha f(\mathbf{v})$$

then the function f is a convex function.

- *7 Convex quadratic programming problem: A programming problem where the minimization target is a convex quadratic function. It is a natural extension of a linear programming problem which is the simplest programming problem, and has numerous applications across many fields. Global optimum solutions are difficult to obtain in general nonlinear programming problems, but exceptionally easy in convex quadratic programming problems. MSM is designed such that various formulations for the acquisition of depth profiles from ARXPS data fall within the category of convex quadratic programming problems.
- *8 Active set method: This is a means of rapidly solving convex quadratic programming problems. It proceeds through a succession of effective constraints to find the optimum solution.
- *9 Kyushu Synchrotron Light Research Center: A radiation light facility established at Tosu City in Saga Prefecture and operated by the Saga Prefecture Industry Advancement Organization with an electron energy capacity 1.4 GeV. It began operation in February 2006.
- *10 SPring-8: Abbreviation for Super Photon ring-8 GeV. A world-class radiation facility with an electron energy capacity of 8 GeV, located in Sayo-gun, Hyogo Prefecture. It began operation in October 1997.

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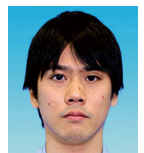
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