Evaluation of MEMS device materials by X-ray fluorescence spectrometers for thin films

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1. Introduction

In the manufacturing process of semiconductor products, thin film inspection methods vary depending on the purpose. For example, optical such as ellipsometers, sheet resistance film thickness meters, step meters, and cross-sectional scanning electron microscopes (SEM) are used for film thickness management. For analysis of composition, X-ray photoelectron spectroscopy (XPS) or other techniques are used.

Among these techniques, X-ray fluorescence (XRF) spectrometers are used in many processes due to the capability to perform simultaneous film thickness/composition analysis non-destructively, with no contact and no sample preparation. The method is applicable to opaque films (metals or nitride films, etc.) and has excellent reproducibility. Special features of wavelength dispersive XRF (WDX; Wavelength Dispersive XRF) analysis are shown below;

1. Analysis of light elements such as B, N and Al
2. Sub-nm (Å) level ultra-thin film analysis
3. Analysis of layered and compound films

Due to these advantages, the use of WDXRF instruments has been increasing in recent years.

2. Applications of WDXRF to MEMS Device Materials

MEMS (Micro Electro Mechanical Systems) devices belong to the subject of the active research and investment in the semiconductor and electronic device fields. Their usage has been increasing for sensors in smartphones, game consoles, automobiles, actuators in printer heads and many others. Areas in which Rigaku WDX products contribute to their characterization include thickness analyses of Al processes for RF devices (SAW/BAW filters; Surface/Bulk Acoustic Wave), and simultaneous thickness and composition analyses of lead zirconate titanate (PZT) processes used as actuator materials. This paper introduces analysis examples of those materials.

3. Instruments

MEMS devices are mainly fabricated on 4, 6 and 8 inch substrates. AZX400 (AZX) and WAFER/DISK ANALYZER 3650 (WDA3650) are used for the analysis. AZX is a sequential-type spectrometer, like members of the ZSX Primus series, and covers analyzing elements from Be to U, making it suitable for research and development. Its large sample chamber allows measurement of wafers up to 300 mm. The WDA3650 is a simultaneous-type spectrometer, like the Simultix series, and is used for in-line monitoring due to its high throughput and ability to perform continuous measurements. The WDA3650 is mainly used for measuring 4, 6 and 8 inch wafers. Both are tube-below type instruments equipped with a 4 kW Rh target X-ray tube. Specifications of the two systems are compared in Table 1.

4. Thin Film FP Method

The thin film fundamental parameter (FP) method in AZX and WDA3650 is well suited for analysis of multilayer materials such as those used in MEMS devices because the evaluation requires analysis of both thickness and composition of compound films[(1)–(3)]. The FP method excels at this analysis and is applicable in the nm to μm order film thickness range. Although standardless analysis is possible in AZX, it is common to use standards for sensitivity calibrations in thin film FP quantification to match results in accurate between multiple instruments.

5. ScAlN Film Thickness and Composition Analysis

Band-pass filters such as SAW/BAW filters are built into communication devices such as smartphones. Conventional devices have many SAW filters using lithium tantalate (LT) or lithium niobate (LN) substrates. WDX spectrometers have been widely used for evaluating the Al (AlCu, AlSiCu) thickness on those substrates. Currently, a plan to use a wide frequency band called "5G" for high-speed and large-capacity data communication is in progress[(4)], and the development of a BAW device[(5)] that can handle a wider frequency band than SAW is also progressing as an RF device. For the BAW filter, Si wafers which are easier to handle than LT or LN can be used as the substrate. AlN (Aluminum nitride) was previously studied as a piezo-electric material, but in recent years ScAlN (scandium aluminum nitride) films are often used[(6)]. Sc concentration is important for product characteristics, and grades of around 10 mol% with respect to Al are used for BAW filters. Qualitative spectra of Sc Kα and Al Kα shown in Fig. 1 were measured with AZX for samples prepared with variety of Sc concentration as

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Table 1. Comparison of AZX and WDA3650.

System	AZX400	WDA3650
Picture		
X-ray tube	4 kW Rh target, tube below type	
Spot size	30, 20, 10, 1, 0.5 mm (Diaphragm)	40 mm, and select 3 from 20, 15, 10, 5 mm (Collimator)
Channels	Scanning channel × 1 (All elements from B–U)	Fixed channel max ×15 and heavy elements scanning channel×1
Applicable wafer size	From 2″ to 300 mm. Also coupons and sputtering targets are available	4″, 6″, 8″ wafers Coupons are also available with the special adaptor
Auto loader	For 8″/300 mm with FOUP or 6″/8″ with cassette (This picture is without loader)	For 4″, 6″, 8″ with cassette
Foot print	890 (D)×1376 (W) mm (Only for main system)	1490 (D)×1120 (W) mm

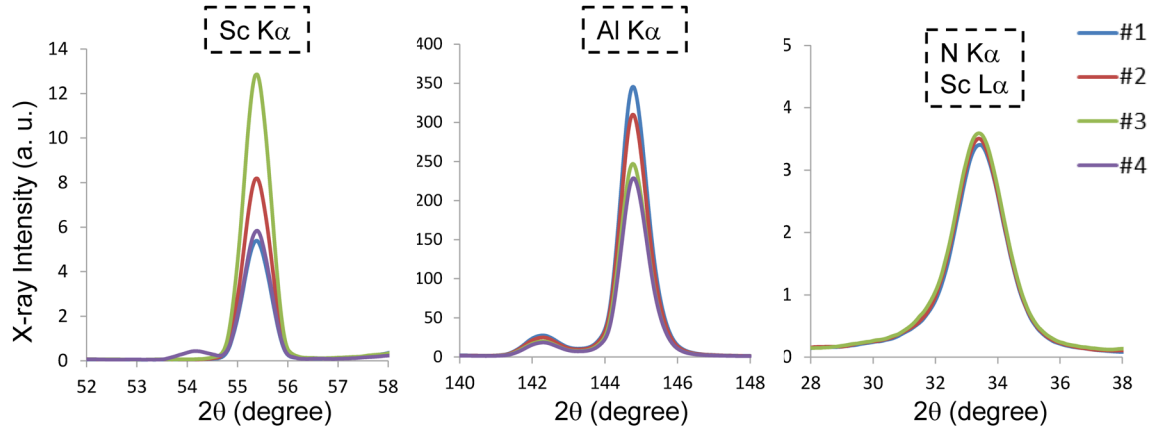

Fig. 1. Qualitative spectra (AZX) of Sc K*α*, Al K*α*, N K*α*.

Table 2. ScAlN film wafers used for analyses.

Wafers	ScAlN thickness (nm)	Sc concentration (mol%)
#1	800	2.5
#2	800	4.5
#3	800	8.5
#4	500	4.5

Note: All values are design ones. Sc concentration obtained by assuming 50 mol% of nitrogen.

Table 3. Measurement conditions (WDA3650).

Elemenet	Sc	Al	Mo
Spectrum	K*α*	K*α*	L*α*
kV-mA	40–80		
Collimator	ϕ 15 mm		
Channel	Fixed	Fixed	Fixed
Analyzing crystal	Ge	TAP	RX4
Detector	S-PC	S-PC	S-PC
Counting time (s)	15		

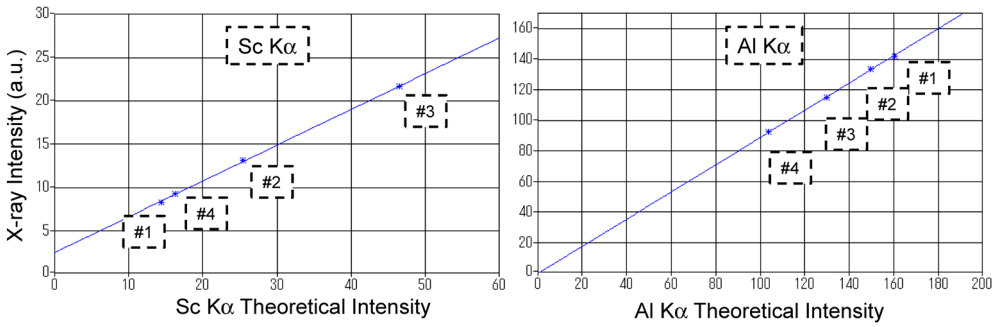

Fig. 2. FP sensitivity calibrations (Sc Kα, Al Kα).

Table 4. 10 times repeatability results (#2).

Component	ScAlN thickness	Sc concentration	Al concentration	Mo thickness
Unit	nm	mol%	mol%	nm
Average	804.2	4.53	45.47	100.0
Max.	805.7	4.55	45.49	100.3
Min.	802.8	4.51	45.45	99.8
Range	2.9	0.04	0.04	0.5
Std. Dev.	0.92	0.012	0.012	0.19
R.S.D.(%)	0.11	0.26	0.03	0.19

Note: 50 mol% of nitrogen was assumed.

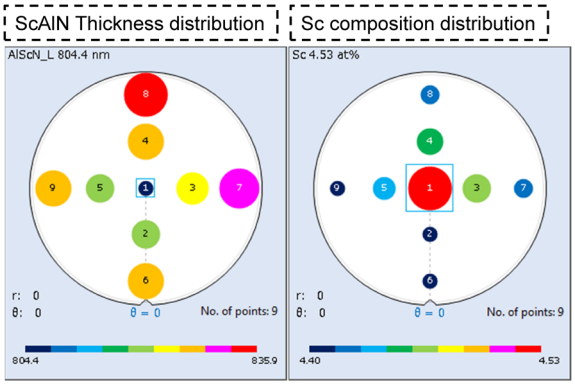

Fig. 3. Bubble charts of ScAlN thickness and Sc concentration (WDA3650 software).

shown in Table 2.

The ScAlN film thickness of BAW filters ranges from about several hundred nm to over 1 μm. In this film thickness range, the Sc Kα and Al Kα intensities depend on both thickness and composition; therefore, information about the thickness is necessary for Sc concentration analysis. In this case, Al Kα is suitable for the thickness/composition simultaneous analyses. Conversely, when Al is not measured, it is necessary to specify the film thickness value. Sc measurement itself can be performed by energy dispersive XRF (EDX), but WDX system has higher precision and excellent resolution capability when performing simultaneous analysis of Al on Si substrate. This is one advantage of WDX over EDX. As shown in the qualitative spectrum in Fig. 1, N can also be analyzed, but it is often not included in control components and is treated in this paper as a fixed component at 50 mol%. When N is analyzed, Sc Lα greatly overlaps with N Kα and therefore it is effective to use the "quantitative FP theoretical overlap correction" to correct for the overlap by Sc Lα.

Using WDA3650, the FP sensitivity calibrations were set up using the samples in Table 2. The measurement conditions are shown in Table 3. Mo is often used as the electrode material in actual products; therefore, Mo films were deposited on the samples and analyzed as a ScAlN/Mo two-layered model. Sc concentration analysis can be performed by other methods such as XPS if analysis is limited to the surface, but XRF is advantageous in that simultaneous analysis of the thickness and the Mo layer are possible.

The FP sensitivity calibrations and 10 times repeatability test results of # 2 (film thickness 800 nm, Sc concentration 4.5 mol%) are shown in Fig. 2 and Table 4.

In this analysis, the film density of ScAlN was assumed to be 3.26 g/cm^3, but a different density can be specified if it is known. As described above, the Sc content is critical for controlling the device characteristics. Table 4 shows that a good repeatability result for the Sc concentration range less than 0.05 mol% was obtained. The ScAlN film thickness and Mo film thickness repeatability results are also very accurate and precise. A nine-point mapping analysis was also performed. The bubble mapping charts of the thickness and Sc concentration are shown on Fig. 3.

As shown in Fig. 3, the ScAlN film was thicker at the outer periphery, while the Sc concentration was found to be higher at the center. ScAlN film is often deposited by sputtering ScAl alloy, but it is generally difficult to uniformly deposit metals of elements with different atomic weights; therefore, in-plane distribution as shown tends to occur. The mapping analysis can therefore be used not only to evaluate the film thickness/composition in the wafer surface, but also to study the characteristics of the process used for film deposition. In AZX and WDA3650, measurement positions can be specified and detailed distribution trends can be visualized by increasing the number of points.

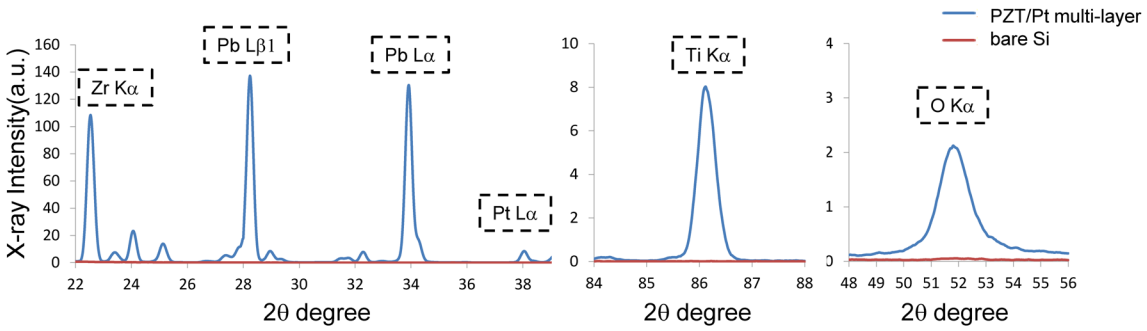

Fig. 4. Qualitative charts of PZT/Pt multi-layer (AZX).

Table 5. Measurement conditions (WDA3650).

Element	Pb	Zr	Ti	Pt
Spectrum	Lα	Kα	Kα	Lα
kV-mA	40−80			
Collimator	ϕ 10 mm			
Channel	Fixed	Fixed	Fixed	Fixed
Analyzing crystal	LiF	LiF	LiF	LiF
Detector	SC	SC	S-PC	S-PC
Counting time (s.)	15			

Table 6. 10 times repeatability results (WDA3650).

Component	PZT thickness	PbO concentration	ZrO_2 concentration	TiO_2 concentration	Pt thickness	Pb/(Zr+Ti)	Zr/(Zr+Ti)
Unit	μm	mol%	mol%	mol%	nm	—	—
Average	3.282	49.42	26.27	24.31	91.8	0.977	0.519
Max.	3.289	49.48	26.35	24.38	92.2	0.979	0.521
Min.	3.272	49.37	26.19	24.23	91.5	0.975	0.518
Range	0.017	0.11	0.16	0.15	0.7	0.004	0.003
Std. Dev.	0.005	0.034	0.041	0.052	0.23	0.0013	0.0009
R.S.D.(%)	0.14	0.07	0.16	0.21	0.25	0.14	0.17

6. Film Thickness and Composition Analysis of Lead Zirconate Titanate Thin Film (PZT)

PZT is known as having ferroelectric characteristics and is used in materials for non-volatile memories, gyroscope and actuator parts in the semiconductor and electronic device fields, for example[7]. In the case of PZT, Pt is often used as the electrode material in the final products. In this paper, a two layer PZT/Pt sample was prepared, and simultaneous analysis of film thickness and composition was carried out.

Qualitative spectra were obtained using AZX (Fig. 4). In addition to the Pb, Zr, and Ti peaks, the Pt peak from the lower layer was detected. Although not included for the analysis in this paper, the O Kα peak was also detected, meaning that information about O concentration is also available.

Quantitative analysis of the sample was performed using the WDA3650. In the semiconductor and electronic device fields, it is often difficult to obtain standard samples with variety of thicknesses and compositions because commercial reference materials may not be available or existing standards may not meet the analyst's budgetary or application needs. AZX is still able to handle such cases by the standardless analysis method. WDA3650 can perform analysis without the need for thin film standards by using metal plates as standards (for example Pb, Zr and Ti pure plates for PZT). Examples of measurement conditions and results for ten times repeat analysis are shown in Tables 5 and 6 respectively.

In this analysis, the film density 7.7 g/cm^3 was used. However, since the film density often depends on the film deposition methods, such as sputtering and sol−gel method, it is desirable to register the actual density if it is known.

The characteristics of PZT are often evaluated by

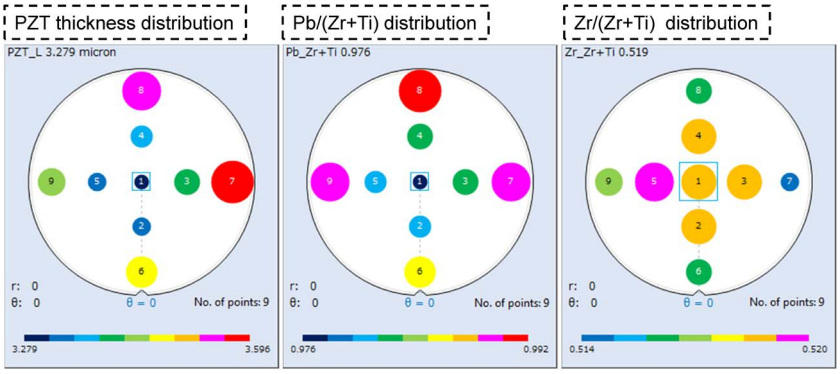

Fig. 5. Bubble mapping chart of PZT film thickness, Pb/(Zr+Ti), Zr/(Zr+Ti) (WDA3650 software).

converting the molar concentration of each element to the ratios of Pb/(Zr+Ti) and Zr/(Zr+Ti). Table 6 also shows these values converted from the concentration, and high precise results with a range less than 0.005 were obtained. Similar to the ScAlN film analysis, a nine-point mapping analysis of the PZT/Pt multi-layer was performed. The bubble mapping charts of PZT film thickness, Pb/(Zr+Ti), and Zr/(Zr+Ti) are shown in Fig. 5.

As shown in the ScAlN film distribution, the PZT sample showed that the film was thicker at the outer periphery. The Pb/(Zr+Ti) value was also high at the outer periphery, while the Zr/(Zr+Ti) value was high at the center.

7. Summary

This paper described film thickness and composition analysis examples of materials for MEMS devices using AZX and WDA3650. In these examples, qualitative analyses were performed with AZX and quantitative analyses with WDA3650, but quantitative analysis with AZX is also possible.

For thin films in the semiconductor and electronic device fields, analysis by WDX has widely been used for the purpose of analyzing light elements such as B and Al. In recent years, the number of applications for the analysis of compound and multi-layered films has been increasing. In addition to the materials for MEMS devices, analysis of devices for the evaluation of advanced materials for non-volatile semiconductor memories such as MRAM and PRAM, and power semiconductors have also been increasing, and it is expected that the activity in these fields will continue to expand in the future.

References

(1) H. Takahara: *Rigaku Journal (English version),* **33** (2017), No. 2, 17–21.
(2) H. Kohno, Y. Araki, Y. Kataoka and M. Murata: *Advances in X-ray Analysis*, **23** (1992), 189–204 (in Japanese).
(3) H. Kohno and H. Kobayashi: *Advances in X-ray Analysis*, **25** (1994), 167–184 (in Japanese).
(4) Ministry of Internal Affairs and Communications: Efforts to realize 5G in 2020 (2018) http://www.soumu.go.jp/main_content/000593247.pdf (in Japanese).
(5) K. Hashimoto: *IEICE Fundamentals Review* Vol. 4 No. 3 (2011), 192–197 (in Japanese).
(6) W. Wang, P. M. Mayrhofer, X. He, M. Gillinger, Z. Ye, X. Wang, A. Bittner, U. Schmid, and J. K. Luo: *Applied Physics Letters,* **105** (2014), 133502.
(7) T. Fujii, T. Naono, A. Mukaiyama, T. Shinkawa, Y. Hishinuma, Y. Li and J. Birkmeyer: *FUJIFILM RESEARCH & DEVELOPMENT,* **No. 59** (2014), 32–37 (in Japanese).
(8) M. Esashi: First MEMS, Morikita Publishing Co., Ltd. (2011) (in Japanese).