Improvement in Linearity of Calibration Curves Using Matrix Components as Modifiers in ETV/ICP-MS and Application for SBT Thin Film

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加熱気化/ICP-MS におけるマトリックス成分補正方法の提案と SBT 薄膜中微量金属への適用

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We established a simple electrothermal vaporization (ETV)/inductively coupled plasma mass spectrometry (ICP-MS) technique without separating analyte elements from a matrix to determine trace metallic impurities of eight elements (Na, Mg, Al, Cr, Mn, Fe, Ni, and Cu) in a Y-1 (strontium (Sr)-bismuth (Bi)-tantalum (Ta)-oxygen (O)) thin film for semiconductor ferroelectric random-access memories. To improve the linearity of each calibration curve (20 pg ml^{-1} – 10 ng ml^{-1}), we added the same concentration of Sr, Bi and Ta to a mixed standard solution as those in the sample solution as a mixed modifier. The recovery percentages obtained by adding 1 ng ml^{-1} of each element to the sample solution were between Al (90%)-Cr (105%). The detection limit (3σ) was 1.9×10^{10} (Mn)– 1.3×10^{12} (Al) atoms cm^{-2} for a Y-1 thin film with a diameter of 150 mm. The proposed method was applied to the real samples to determine the eight metallic elements (10^{11} – 10^{13} atoms cm^{-2}).

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1. Introduction

Determining metallic impurities in semiconductor materials is known to be very important, because of their influence on electric properties, p - n junction leakage and the degradation of the oxide breakdown voltage et al.^{(1),(2)} For this determination, furnace atomic absorption spectrometry (FAAS),^{(3)–(5)} inductively coupled plasma mass spectrometry (ICP-MS)^{(6)–(9)} and total-reflection X-ray fluorescence analysis (TRXF)^{(10)–(12)} are often been used. Despite these methods, a simple determination method for trace metallic impurities is required to develop new semiconductor materials, improve their properties and achieve high product yields for semiconductor devices. There have been a few reports on the analysis of ferroelectric materials^{(1),(13)} and its thin film⁽²⁾ for semiconductor ferroelectric random-access memories and ferroelectric random-access memories have been receiving attention as a form of nonvolatile memory.⁽¹⁴⁾ Yabuki reported on the analysis of metallic impurities in metal-oxide thin films using precipitation separation/nebulizer ICP-MS and FAAS.⁽²⁾ Using these methods, it is possible to sensitively and accurately measure analyte elements.⁽²⁾ However, these methods are time consuming due to the process of separating analyte elements from the matrix.⁽²⁾

As a ferroelectric material BST (referred to as Y-1 hereafter) is composed of strontium (Sr), bismuth (Bi), tantalum (Ta) and oxygen (O),⁽¹⁵⁾ trace metallic impurities exist with the matrices Sr, Bi, and Ta in the Y-1 sample solution.⁽¹⁾ In the nebulizer type ICP-MS, Fe is one of the elements that is influenced by molecular ions such as $^{40}\text{Ar}^{16}\text{O}$ due to argon, solvents et al. Using cool plasma in this method, the Fe ion intensity is depressed by the matrix. Avoiding this type of depression by diluting the elements results in a reduction in the sensitivity of the real measurements. On the other hand, electrothermal vaporization (ETV)/ICP-MS is available for mul-

tiemental measurements of the micro sample solution^{(6)–(8)} and it also avoids the spectral influences of $^{40}\text{Ar}^{16}\text{O}$ on the ^{56}Fe ion intensity that occurs in the nebulizer type ICP-MS. In particular, for the high matrix concentration of the sample solution, using the nebulizer type ICP-MS for a long time measurement, an introduction system such as the skimmer cone is probably plugged due to the matrix components, while the problems associated with the introduction system do not occur in ETV/ICP-MS because the amount of the sample introduction to ICP in the ETV type is a one-dozen less than that in the nebulizer type.

In the meantime, with ETV/ICP-MS, using a “matrix modifier” is beneficial. The matrix modifier can be classified as a physical modifier or a chemical modifier according to the manner in which it functions. As for the former case, it functions as a carrier for preventing the analyte vaporized in the ETV chamber from condensing in the sample-introduction system leading to the ICP. Improved analysis sensitivity and linearity of the calibration curve due to this function, have been reported.^{(16)–(20)} On the other hand, as for the latter case, it has been reported that lowering the vaporization temperature of the matrix but raising the vaporization temperature of the analyte improves the inspection and analysis sensitivity of the separation technique.^{(19)–(23)} In establishing the analysis method, although previous reports have become the standard for selecting the modifier, fundamentally, it is necessary to select the suitable modifier for the matrix and the analyte on a case-by-case experimental basis.

The purpose of this work is to establish a simple ETV/ICP-MS without separating analyte elements from a matrix before measurements. We examined a matrix modifier for determining a Fe impurity in the Y-1 thin film, and obtained a calibration curve with good linearity for Fe by adding the same concentration of Sr, Bi and Ta to a mixed standard solu-

Table 1. ETV Operating Conditions

Stage	Temperature / °C	Ramp / s	Hold / s
Drying	90	10	0
	120	15	30
	100	0	20
Vaporization	2400	0	5
Cleanup	2800	0	3

Carrier Ar flow rate 0.9 l ml⁻¹, Sample injection volume 25 μ l.

tion as those in the sample solution. Furthermore, we obtained calibration curves with good linearity for the other seven elements (Na, Mg, Al, Cr, Mn, Ni, and Cu) in the same manner. The proposed method was applied to determine the eight metallic elements (10^{11} – 10^{13} atoms cm⁻²) in the ferroelectric film samples on a silicon (Si) wafer with a diameter of 150 mm.

2. Experimental

2.1 Reagent and sample

We used the same reagents and water as in the previous work²⁴⁾ except for the Sr, Bi and Ta standard solutions (1000 μ g ml⁻¹ of each element) from SPEX (CertiPrep Inc., Metuchen, N. J., USA). We deposited Y-1 thin film samples: SrBi_{2.1}Ta_{1.9}O_x (ca. 200 nm thickness)/Pt/SiO₂/Si-substrate (diameter of 150 mm) on a Si wafer by a metal-organic decomposition (MOD) method using alcoxide.

2.2 Apparatus

We employed an ICP mass spectrometer, a furnace for the ETV and a autosampler in the previous work,²⁴⁾ and employed an ICPS-8000, an inductively coupled plasma-atomic emission spectrometry (ICP-AES) system (Shimadzu, Kyoto) for determining Sr, Bi, and Ta in the thin film samples.

2.3 Procedure

We set a Y-1 thin film sample on Si wafer was set in the decomposition vessel. Five milliliters of a mixed acid (HF : HNO₃ = 1 : 1) were added to the film sample, and we decomposed the sample using an illuminating IR lamp. We then diluted the recovered solution to 500 ml with water. The 25 μ l of the sample solution was injected into the graphite boat, after which we measured the ion intensities from group 1 (²³Na, ²⁴Mg, ²⁷Al, ⁵³Cr and ⁵⁵Mn) to group 2 (⁵⁶Fe, ⁶⁰Ni, ⁶³Cu) using the operating conditions for ICP-MS in the previous work²⁴⁾ and using the operating conditions for ETV shown in Table 1. In order to cancel the decrease of the analyte element ion intensities due to transport loss using only mixed standard solutions, we matched the mixed standard solutions for the calibration curve to the matrices of the sample solution.

The treatment for preparing the sample solution and the standard solution was carried out on a class-100 clean bench. The ETV/ICP-MS measurements were carried out in a class-1000 clean room.

3. Results and discussion

3.1 Effect of the concentration of Sr, Bi, Ta and Pd on Fe ion intensities

To select a matrix modifier, we examined the effects of the concentration of the Y-1 matrix components Sr, Bi, Ta, and a Pd matrix modifier used in the previous work²⁴⁾ on Fe ion intensities at the concentration of Fe 1 ng ml⁻¹. The results are shown in Fig. 1. The behavior of Fe ion intensity can be

Fig. 1. Effect of the concentration of strontium, bismuth, tantalum and palladium on iron ion intensity. Fe 1 ng ml⁻¹, ■ Strontium, ● Palladium, ▲ Tantalum, ◆ Bismuth.

explained in terms of the transport efficiency of Fe ions and the atomic-weight effect²⁵⁾ of coexisting elements. In the case of coexistence of Sr and Pd at concentrations up to 10 μ g ml⁻¹, Fe ion intensity increases as a result of improved transport efficiency accompanying the physical modifier effect of these two elements. However, it is considered that the decrease in Fe ion intensity due to the atomic-weight effects of Sr and Pd is even stronger. Moreover, in the case of coexistence of Sr at a high concentration, namely, 100 μ g ml⁻¹, the decrease effect on Fe ion intensity due to the atomic-weight effect of Sr decreases the Fe ion intensity that had been increasing up to that concentration. In the case of coexistence of Pd at a concentration of 100 μ g ml⁻¹, the decrease in Fe ion intensity due to the atomic-weight effect of Pd is large, and the Pd-addition effect is not shown. Moreover, it is confirmed in Fig. 1 that as the mass number of the coexisting element increases, the decrease in Fe ion intensity gets bigger in approximate accordance with the atomic-weight effect. The reason for the slight increase in Fe ion intensity under coexistence of Ta at concentration of 100 μ g ml⁻¹ in comparison with the Fe ion intensity at Ta concentrations up to 10 μ g ml⁻¹ is unknown. Furthermore, as for the atomic-weight effect,²⁵⁾ in the sample-introduction system between the ICP and the mass spectrometer, the analyte ions collide with coexisting elements with higher mass number, and go astray from their primary trajectory, thereby decreasing the introduction efficiency of the analyte ions into the mass spectrometer (i.e., ion intensity decrease). The influence of coexisting elements with high mass number on the ion intensity is therefore big.

From these results, we did not use Sr, Bi, Ta, and Pd as a modifier, because the positive effects of adding the Pd modifier as shown in the previous work²⁴⁾ were not observed this time.

3.2 Effect of the concentration of synthetic Y-1 components on Fe ion intensities

We prepared mixed standard solutions containing Sr, Bi, and Ta in concentration (μ g ml⁻¹) ratio (Sr 1: Bi 5: Ta 4) adjusted to Y-1 composition, and examined the effect of the mixed standard solution on Fe ion intensities at the concentration of Fe 1 ng ml⁻¹. The results are shown in Fig. 2. We observed a larger increase of Fe ion intensity at a concentration range (Sr: 0.1–1 μ g ml⁻¹, Bi: 0.5–5 μ g ml⁻¹, Ta: 0.4–4 μ g ml⁻¹). Thus, we used Sr 1 μ g ml⁻¹, Bi 5 μ g ml⁻¹ and Ta 4 μ g ml⁻¹ as a mixed modifier in this work.

3.3 Calibration curve, recovery, and detection limit

The correlation coefficient, recovery percentage, and detec-

Fig. 2. Effect of the concentration of synthetic Y-1 components on iron ion intensity. Fe 1 ng ml⁻¹.

Fig. 3. Calibration curve for iron.

tion limit were examined using mixed standard solutions ranging from 20 pg ml⁻¹ to 10 ng ml⁻¹ that contained Sr (1 μg ml⁻¹), Bi (5 μg ml⁻¹), and Ta (4 μg ml⁻¹) as the mixed modifier. As shown in Fig. 3, the calibration curve obtained for Fe was linear and had a high correlation coefficient of 0.999. The calibration curves for the other seven elements obtained in the same manner as that for Fe were also linear, with high correlation coefficients of 0.998 (Cr) and 0.999 (each of other six elements), although these results are not shown here. Incidentally, as described in the previous work,²⁴⁾ using only mixed standard solutions without adding a modifier, significant ion intensity losses were observed in the eight calibration curves obtained. To certify the accuracy of this method, we examined the recovery percentage of the eight elements. One nanogram per milliliter of eight elements was added to the real sample solution. Good recovery percentages of 93% (Na), 91% (Mg), 90% (Al), 105% (Cr), 97% (Mn), 100% (Fe), 94% (Ni), and 104% (Cu) were obtained. The detection limits (3σ) are shown in Table 2. The detection limits were between Mn (0.6 pg ml⁻¹, 1.9 × 10¹⁰ atoms cm⁻²)-Al (20 pg ml⁻¹, 1.3 × 10¹² atoms cm⁻²). Most of the detection

Table 2. Detection Limits (× 10¹¹ atoms cm⁻²)

Analyte Element	ETV/ICP-MS	
	pg ml ⁻¹	atoms cm ⁻² *
Na	3	2.2
Mg	2	1.4
Al	20	13
Cr	20	6.6
Mn	0.6	0.19
Fe	10	3.1
Ni	6	1.7
Cu	5	1.3

*Thin film sample with diameter of 150 mm

Table 3. Analytical Results of Trace Impurities in Ferroelectric Y-1 Film Samples (× 10¹² atoms cm⁻²)

Analyte element	Sample A*	Sample B*
Na	3.9	7.4
Mg	1.5	3.9
Al	7.4	13
Cr	2.7	2.2
Mn	0.21	0.48
Fe	1.1	6.3
Ni	0.78	0.73
Cu	0.48	1.0

*Thin film sample with diameter of 150 mm, Sample A: developed prototype, Sample B: a manufacturer's product

limits were less than those calculated from minimum limits of determination (Ni: 1 × 10¹⁰ atoms cm⁻², Mn: 2 × 10¹⁰ atoms cm⁻² et al.) of Yabuki.²⁾

3.4 Application

The analytical results of real ferroelectric film samples (sample A: developed prototype; B: a manufacturer's product) with a diameter of 150 mm are shown in Table 3. The values for Al were approximately 10¹³ atoms cm⁻² in samples A and B, while the values for Mn were approximately 10¹¹ atoms cm⁻². The Na and Fe values were approximately 10¹³ atoms cm⁻² in sample B. Except for these results, the values of Na, Mg, Cr, Fe, Ni and Cu were approximately 10¹² atoms cm⁻². It is considered that the difference in impurity concentrations of samples A and B is due to differences in the purity of the film raw materials and film-formation conditions. From the above results, an improvement in the impurity level occurred, resulting in a Y-1 thin film of good quality. And in the case of samples 1 to 5, the time needed for this analysis method is about half that needed for Yabuki's method.²⁾ The proposed method would be especially useful for analyzing a lot of samples having the same composition because the determination for the composition of one sample is only required.

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