DETERMINATION OF TRACE IMPURITIES IN TANTALUM OXIDE FILMS BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY COMBINED WITH ION EXCHANGE

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Abstract - The determination of trace metals has been carried out by inductively coupled plasma mass spectrometry. A tantalum sample was dissolved and the influence of the matrix was rejected by anion exchange. Detection limits were 0.006-0.02 wt.ppm. This method is being used for the analysis of tantalum oxide films.

Key words tantalum, anion exchange, inductively coupled plasma mass spectrometry

Inductively coupled plasma mass spectrometry (ICP-MS) has been extensively employed for trace metal analysis and metal isotopic analysis in many fields. There are applications in this analytical method using laser ablation and electrothermal vaporization. Tantalum oxides (Ta₂O₅) are used as insulation films in dynamic random access memories and as capacitor conducting material in hybrid integrate circuits. It is important to measure the impurity contents in Ta₂O₅ films, because impurities in the films are known to affect the electrical characteristics significantly.

In this work, the purpose of the investigation is to establish a sensitive and accurate determination method for detecting impurities in Ta₂O₅ films by using an ion exchange method and inductively coupled plasma mass spectrometry (ICP-MS).

EXPERIMENTAL

Apparatus The ICP-MS instrument for used was SPQ-6500 (Seiko Instrument Inc., Tokyo). The operating conditions are shown in Table 1. The ion lenses and mass resolutions were set by tuning so as to yield maximum responses for Co, Ba, and Pb.

Reagents Stock solutions were prepared by diluting a single element stock solution (for use in atomic absorption spectrometry, Kanto Chemical Co. Inc.). Working standards were obtained by mixing aliquots of 10 ppm stock solutions. The resin used was an anion exchange of MCL GEL CA08P of 75- to 150-mesh particle size, supplied by Mitsubishi Chemical Co. Inc., Japan. All of the acids used were of TAMAPURE-AA-100 (Tama Chemical Co. Inc., Japan).

TABLE 1. Operating conditions for ICP-MS instrument

Plasma power	1.2 kW
Reflected power	< 5 W
Carrier gas flow rate	0.51/min
Plasma gas flow rate	161/min
Auxiliary gas flow rate	1.01/min
Sampling depth	15 mm
Pressure in spectrometer	
Vacuum stage 1	250 Pa
Vacuum stage 2	10 ⁻³ Pa
Vacuum stage 3	10 ⁻⁴ Pa
Dwell time	100 ms
Accumulation time	50
Channel width	5

Procedure Sample wafers with a tantalum oxide film were dissolved by 10 ml of 6 M hydrofluoric acid, and then added to 1 ml of conc. nitric acid. The dissolved solution was loaded into an anion exchange column containing 5 ml resin which had been preconditioned with a 0.2 M hydrofluoric- 2 M nitric acid solution. Next, the mixed solution with the same concentration as the preconditioned solution was loaded in the same column. All the effluents

were reserved for determining the impurities. 4 M perchloric acid was added and then evaporated to a dry state till the perchloric acid fumed. The residual was dissolved with 5 ml of 1 M nitric acid. Finally, the solution was measured by ICP-MS. All the pretreatment was done in a clean room which was cleaner than class 10000.

RESULTS AND DISCUSSION

A tantalum sample is one of the most difficult to decompose by an acidic solution, so hydrofluoric acid was selected to dissolve the sample. Because it has been reported that signal intensities were suppressed by heavy matrix elements, it was necessary to reject the tantalum matrix[1]. The authors chose the procedure of anion exchange to solve this problem. Tantalum is hardly eluted from the anion exchange column by a nitric-hydrofluoric acid mixed solution[2]. Finally, a 0.2 M hydrofluoric- 2 M nitric acid solution was used to separate the tantalum matrix. In this concentration, other impurities were eluted completely by a 50 ml solution. This system offered the advantage over nitric- hydrofluoric acid separation in that most impurities could be eluted without a change in the acid mixture composition. In order to examine the feasibility of the tantalum analysis method a mixture solution was prepared and the recovery measured, resulting in more than 90% recoveries for most elements within this effluent volume.

The detection limits were defined as three times the standard deviation of the blank value. This method gave a range from 0.006 to 0.02 wt.ppm. The difference in these values were based on environmental contamination from measurement, memories of sampling and skimmer cone, and overlapping of molecular ion peaks. The authors applied this method to Ta2O5 films. The analytical results are summarized in Table 2. These values are 4 individual repetitions. The tantalum oxide films were about 1200 Å thick, so the theoretical weight was 15 mg. Because of the variable film thickness, the precisions of the resulting values were not constant. This method has been found to be highly effective for removing matrix constituents, and to be able to measure impurities in Ta2O5 films simultaneously.

TABLE 2. Results of quantitative determination of impurity elements in tantalum oxide films (wt.ppm)

Sample	Ti	Mn	Zr	Nb	W	Pb
A	7.7	0.01	0.31	4.1	0.12	0.15
	6.3	0.01	0.22	4.3	0.15	0.12
B	5.9	0.02	0.13	1.3	0.06	0.17
	3.8	0.01	0.22	1.0	0.13	0.26

REFERENCES

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