ICP SPECTROCHEMICAL ANALYSIS OF FINE CERAMICS CONVERTED TO THIN FILM BY RF SPUTTERING

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Abstract - RF sputtering technique has been applied to the determination of major and minor elements in sintered fine ceramics. Alumina, zirconia and PLZT converted to thin films on the quartz plate are dissolved in hydrochloric or sulfuric acid, and analysed by ICP-AES. Analytical results are agreed with reported values of the original ceramic target after optimization of RF power, kind of sputtering gas and its pressure for each ceramics.

Key word ICP determination, fine ceramics, sputtering, thin film

Many kinds of sintered fine ceramics have been used in wide field, because of their high solidity and high resistance to chemicals. But these excellent characteristics are not convenient for chemical analysis. Some powdered ceramics are dissolved in acids at high temperature and pressure, but almost all solid ceramics cannot be dissolved by acid digestion or alkali fusion. And the crush of the solid ceramics causes contamination from the used tools. In this report, a sputtering technique is applied to the determination of major and minor elements in sintered fine ceramics without contamination.

EXPERIMENTAL

Ceramic sample Pure alumina (99 % up), mixed alumina involving about 3 % of calcia and magnesia, stabilized zirconia involving about 6 % of yttria (Kojundo Chemical Laboratory) and PLZT (Kyodo International) were sintered as a sputtering target respectively.

Sputtering method Anelva SPF-210 was used for RF sputtering. Pure argon and mixed argon with 30 % of oxygen were examined as a sputtering gas. Gas pressure, RF power and sputtering time were optimized for each ceramics.

Sputtered sample was collected on the quartz plate (25 mm x 25 mm x 2 mm). Dissolution and ICP analysis Mixed alumina and PLZT samples converted to the thin films were dissolved in (1+1) hydrochloric acid in Teflon beaker on the hot plate, and pure alumina and stabilized zirconia were decomposed with (1+3) sulfuric acid in sealed Teflon vessel at 230 °C for 16 hr(1). Seiko SPS1200VR ICP spectrometer was used for the determination. Analytical results were obtained as a typical oxide, and each contents were calculated on the basis of the total amount of the obtained oxides.

RESULTS AND DISCUSSION

Decomposition and detection limit The mixed alumina sample after crushing using an agate mortar and pestle was not dissolved in hydrochloric acid, but the converted sample to thin film was easily dissolved. The converted PLZT was also dissolved in hydrochloric acid. On the other hand, converted pure alumina and stabilized zirconia samples were only decomposed in sulfuric acid using sealed Teflon vessel. Detection limits, which were in the level of 0.002 - 0.01 % assuming that the total amount of obtained oxides was 8.0 mg, were almost same in both dissolution methods, except for silicate. As silicon was slightly dissolved from the quartz plate in hydrochloric acid, the detection limit was inferior to those of other oxides. Further, silicate could not be determined in sulfuric acid decomposition, because approximate 1 mg of the quartz plate was dissolved.

TABLE 1. Optimized sputtering conditions

	Pure and mixed alumina	Stabilized zirconia	PLZT
Incident power (W)	670	600	300
Plate voltage (kV)	4.0	4.0	3.0
Plate current (mA)	190	180	120
Sputtering gas	Ar+O ₂	Ar+O ₂	Ar+O ₂
Pressure (Pa)	0.8	2	11
Sputtering time (hr)	3	1	1
Collected amount (mg)	Mix 8.46, Pure 8.75	6.78	8.21
RSD (%)	1.4 5.3	2.5	3.2

Effect of sputtering gas and RF power The amount of the collected samples in pure argon sputtering was more than that in mixed argon with 30 % oxygen. But the contents of some oxides were different from those in original target, where selective sputtering should be carried out. In the case of mixed alumina, MgO content significantly decreased and CaO slightly increased with the increase of RF power in pure argon sputtering. Similar selective sputtering with pure argon was also observed in the case of PLZT. Then, mixed argon was used as a sputtering gas later. The pressure of the mixed argon did not affect the contents in two kinds of alumina and stabilized zirconia. However, in the case of PLZT, the content of PbO decreased, and of TiO₂ and ZrO₂ increased with the increase of the pressure. The total amounts of collected samples were increased with the increase of the RF power in all ceramics. The contents of TiO₂ in PLZT decreased at low pressure and increased at high pressure with the increase of RF power.

Analytical results Sputtering conditions were optimized to prepare thin film whose composition was the same of the original target. Final sputtering conditions and collected amounts with RSD for each ceramics are summarized in TABLE 1. Sputtering time was decided to get about 7 - 8 mg of the sample. The RSD in the collected amounts was 1 - 5 %. Analytical results and reproducibilities from obtained 3 samples in optimized conditions are shown in TABLE 2. Analytical results by proposed method were agreed with reported values by the target makers. RSDs were approximately 1 % for major, 1 - 3 % for minor and 3 - 8 % for trace elements, respectively.

TABLE 2. Analytical results (%)

	Mixed alumina			Pure alumina			Stabilized zirconia			PLZT		
	Pro.*	RSD	Rep.**	Pro.	RSD	Rep.	Pro.	RSD	Rep.	Pro.	RSD	Rep.
Al ₂ O ₃	94.3	0.9	Maj.	99.8	1.0	Maj.	0.03	9.4	0.01	0.19	6.1	
CaO	2.95	1.5	3.1	0.03	5.2		0.29	2.9	0.1	0.06	3.5	
MgO	2.67	1.3	3.0	0.01	4.3		0.05	4.7	0.03	0.01	5.9	
SiO ₂	0.08	18		--	--	0.14	--	--		0.28	15	
Fe ₂ O ₃	0.02	4.7		0.03	6.3	0.10	0.03	5.6	0.01	0.01	5.7	
Na ₂ O	0.03	5.6		0.08	8.4	0.14	0.04	7.2		0.02	6.7	
PbO										63.1	1.1	63.0
La ₂ O ₃										3.98	1.5	3.91
ZrO ₂							93.1	1.1	Maj.	22.7	0.8	24.4
TiO ₂							0.02	5.5	0.02	9.58	0.9	8.64
HfO ₂							0.59	3.5	1.2	0.38	3.8	
Y ₂ O ₃							5.92	0.7	5.5			

* Pro: analytical value by proposed method

** Rep: reported value by the target maker

Proposed sputtering technique is effective for the determination of major, minor and trace elements in sintered fine ceramics after optimization of the sputtering conditions. And the thin film analysis is also useful for the discussion on the sputtering mechanism and for the quality control in semiconductor industry.

REFERENCES

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