RADIO-FREQUENCY GLOW DISCHARGE ATOMIC EMISSION AND MASS SPECTROMETRY

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Abstract - Grimm-type glow discharge sources were constructed for excitation sources of atomic emission and mass spectrometry. Radio-frequency discharge was used for the excitation of nonconducting materials. Atomic emission and mass spectra of sintered ceramics (alumina, zirconia and silicon nitride) were measured under various operating conditions, and the effects of parameters such as rf power, gas pressure and sample thickness on the spectra were studied.

Key words glow discharge, radio frequency, emission spectrometry, mass spectrometry, ceramics

Interest in the glow discharge as an excitation source for the direct analysis of solid samples has grown recently in atomic emission and mass spectrometry. Especially, radio-frequency (rf) glow discharges are attractive owing to the fact that nonconducting solid samples can be directly excited. Winchester *et al.*[1] recently reported characteristics of an rf glow discharge emission source for the analysis of conducting and nonconducting samples. Donohue and Harrison[2] and Duckworth and Marcus[3,4] described rf glow discharge ion sources for a sector-type and a quadrupole mass spectrometer, respectively. In this paper, we will describe Grimm-type rf glow discharge sources for emission and mass spectrometry of nonconducting samples. The geometries of the sources are similar for both methods allowing the external sample mount. In the mass spectrometry, the source was interfaced to a commercial mass spectrometer that was used for inductively coupled plasma mass spectrometry (ICP-MS)[5]

EXPERIMENTAL

Instrumentation A schematic diagram of the glow discharge source for mass spectrometry is shown in Fig. 1. This source can be used for both of the dc and rf glow discharges. Flat samples with diameters of larger than 15 mm can be externally mounted by simply pressing them against an O-ring in the cathode plate. The rf power was supplied to a copper disk in contact with the back of the ceramic sample and the rf ground side was connected to the anode: the cathode plate floated electrically from the rf power. The device was bolted onto the ICP mass spectrometer interface plate in place of the sampling cone. The anode ring made of stainless steel with 9 mm i.d. also functions as a sampling restrictor. The parts other than the anode ring were made of brass. Argon gas was fed into the chamber through a 0.2 mm gap between the sample surface and the anode ring. The vacuum pump (mechanical) in the first stage of the ICP mass spectrometer was operated less than 1 min only after the sample was changed: the vacuum in the discharge chamber was maintained by the evacuation through the skimmer orifice (0.6 mm). The discharge

Fig. 1. Schematic diagram of glow discharge source

pressure, therefore, was controlled by varying the Ar flow rate. The design of the source for emission spectrometry was similar to that described above but the anode ring was made of brass with 5 mm i.d. and a silica optical window was attached to the chamber facing to the sample at a distance of c.a. 45 mm from it.

The rf power supply used was an RFS-002A (ULVAC, 13.56 MHz, 200 W) equipped with a matching box, MB-002M. The matching circuit was modified as shown in Fig. 2 to ignite the discharge easier. The matching was adjusted every time the operating conditions were changed to reduce the reflected power less than 0.5 W. A grating monochromator, Nikon P-250 (f=250 mm, 1200 g/mm grating) was used to measure the emission spectra. The ICP mass spectrometer used was an SPQ-6100A (Seiko Instr. Inc.) without modification including the copper skimmer. The ion lens voltages, however, was readjusted for the glow discharge.

Fig.2. Matching circuit

Samples Sintered ceramic samples (alumina, zirconia and silicon nitride) in a disk form were obtained from Government Industrial Research Institute, Nagoya and Japan Fine Ceramics Center. The samples were polished with diamond paste and rinsed with acetone prior to use.

RESULTS AND DISCUSSION

Emission spectrometry

Spectra An example of the emission spectra of alumina is shown in Fig. 3. A few emission lines of Al sputtered from the sample are identified, though most of the prominent lines are Ar lines and OH bands. The latter probably arose from moisture in the sample and water impurity in argon. Although the emission lines of the major components, Al, Zr and Si were clearly observed in alumina, zirconia and silicon nitride, respectively, the lines of the minor components of the samples were difficult to identify because of the insufficient sensitivity.

Fig. 3. Emission spectra of alumina

Effect of operating conditions With an alumina sample, the effects of various operating conditions on the emission intensities of the Al 396.1 nm and Ar 407.2 nm lines were examined. The intensities of both lines increased with increasing rf power from 10 to 40 W at a discharge pressure of 1 Torr. Since the Al line increased more rapidly than the Ar line, the intensity ratio, I_{Al}/I_{Ar} , also increased almost linearly with the rf power.

The effect of the discharge pressure on the emission intensities is shown in Fig. 4. The pressure was measured with a Pirani gauge attached to the vacuum line at a distance of c.a. 30 cm from the discharge chamber. Therefore, the pressures do not necessarily show the true values in the

Fig. 4. Effect of pressure

discharge chamber. The Al line intensity is highest at a pressure of 0.8 Torr and rapidly decreases with increasing pressure. The behavior of the Ar line is similar but its peak slightly shifts to a higher pressure. Therefore, the ratio, I_{Al}/I_{Ar} , increases with decreasing pressure. The optimum discharge pressure seems to be in the range of 0.8-1.0 Torr. These values are significantly lower than those described by Winchester et al.[1] who recommended 6-10 Torr. The difference might be caused by the position of the gauge.

The effect of the sample thickness is shown in Fig. 5 at an rf power of 30 W and a pressure of 1 Torr. Since the rf power is fed from the back of the sample disk, its thickness affects the discharge condition and then the emission intensity. As shown in Fig. 5, the intensities of both the Al and Ar lines decrease with the thickness. As the Al line decreases more rapidly than the Ar line, the intensity ratio also decreases with increasing thickness.

Mass spectrometry

Spectra An example of the mass spectra of zirconia measured at 30 W and 0.4 Torr is shown in Fig. 6. Partially scale expanded spectra are also shown. Zirconium isotopes and their oxide peaks are clearly observed. The intensities of doubly charged and oxide ions of Zr are about 10 % of those of Zr. The peaks at masses of 12, 14, 16, 17, 18 and 19 are C, N, O, OH, OH₂ and OH₃, respectively. Intensities of OH⁺, OH₂⁺ and OH₃⁺ ions which contain hydrogen tend to scatter from sample to sample, probably because these ions partly arose from moisture in the sample. The sample shown in Fig. 6 contains 0.44 % of Al and 3.56 % of Y, and their peaks are observed at masses of 27 and 89, respectively. Hafnium isotopes are also observed at masses of 176-180. Peaks at 63 and 65 amu belong to Cu, which may originate from the skimmer.

Mass spectra of alumina and silicon nitride samples were also measured. Intensities of the Al⁺ ions for alumina and the Si⁺ ions for silicon nitride were about the same level to those of Zr isotopes for zirconia under comparable operating conditions. Other background ion peaks were similar to each other for these samples.

Effect of rf power Variation of the intensities of Zr⁺, Al⁺, Y⁺ and Hf⁺ is shown in Fig. 7 as a function of rf power. Intensi-

Fig. 5. Effect of thickness

Fig. 6. Mass spectra of zirconia

Fig. 7. Effect of rf power

ties of all the ion peaks increase with increasing rf power from 10 to 40 W as is the case in the emission spectra. The slopes, however, slightly decrease above 30 W. The same trend was observed at different pressures in a range from 0.16 to 0.6 Torr. The intensity ratios of these ions to Zr^+ are not necessarily constant.

Effect of pressure Variation of the intensities of Zr^+ , Al^+ , Y^+ and Hf^+ as a function of the discharge pressure at an rf power of 30 W is shown in Fig. 8. The pressure of the discharge chamber was measured with a Pirani gauge equipped in the ICP mass spectrometer. Although the intensity of Zr^+ increases at pressures lower than 0.3 Torr, the operation of the glow discharge at this range is not convenient, because the intensities of the background ions such as Ar^+ , O^+ and OH^+ extremely increase with decreasing pressure. Moreover, oxide and doubly charged ions tend to increase in this region. The optimum discharge pressure seems to be in the range of 0.4-0.6 Torr.

Effect of sample thickness Variation of the intensities of Zr^+ , Al^+ , Y^+ and Hf^+ as a function of the sample thickness is shown in Fig. 9. These samples were prepared by slicing a sintered zirconia block but different one that was shown in Figs. 6-8. As in emission spectrometry, intensities of the sample component ions decrease with increasing sample thickness. Since the intensity ratios of the minor component ions to Zr^+ also vary with the thickness, the sample thickness should be prepared as same as possible in the analysis.

In conclusion, the rf glow discharge emission and mass spectrometry is quite attractive for the determination of impurities in nonconducting samples such as ceramics. In emission spectrometry, however, the sensitivity seems to be too low to determine trace impurities. In the GD mass spectrometry with dc mode, it was reported that the sensitivity was appreciably improved by positive biasing the anode with respect to ground [6]. If this means are applied in the rf glow discharge, the sensitivity will be much improved. The works in this direction are progress in our laboratory.

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Fig. 8. Effect of pressure

Fig. 9. Effect of thickness