ANALYSIS OF ZIRCONIUM NITRIDE FILM BY INDUCTIVELY COUPLED PLASMA EMISSION SPECTROMETRY

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Abstract - After digestion of zirconium nitride film in hydrofluoric acid without loss of nitrogen, zirconium and nitrogen were determined by inductively coupled plasma-atomic emission spectrometry with internal standardization and titration method using an autotitrator respectively. The molar ratio of zirconium to nitrogen was 1:0.99 and the RSD for 4 samples was 0.49%.

Key words zirconium nitride, ICP-AES, titration

The nitrides are widely used as refractory, wear and corrosion resistant surface coating. Since the properties of nitrides depend strongly on their stoichiometry, quantitative analysis has become important. Although nitride film has been analysed using nuclear analysis[1-2], Auger electron analysis (AES)[3] and electron microprobe analysis[4], such methods are expensive and/or require standard ZrN film sample. In this work, zirconium and nitrogen in ZrN film, which was deposited on stainless steel substrate, were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) with internal standardization and titration method using an autotitrator respectively

EXPERIMENTAL

After digestion of nitride in acid in a glass or Teflon 100ml beaker, NH_3 was distilled with a distillation apparatus[5] and collected in 50ml of 0.025 or 0.05M H_2SO_4 . In the other case, nitride was fused with alkali flux in a nickle crucible, and evolved NH_3 was swept by a stream of argon into 50ml of 0.05M H_2SO_4 . The solution was titrated with carbonate-free 0.05 or 0.1M NaOH using an autotitrator (HIRANUMA SANGYO Co., Ltd. COMTITE-7). An ICP-AES instrument used in this work was SPS1200VR (SEIKO Instruments Inc.). In the investigation of digestion, ZrN powder (RARE METALLIC CO., LTD.) was used. By vacuum arc ion-plating method, ZrN film was prepared, which was deposited on one side of 17mm by 17mm square-shaped plate made of stainless steel. The weight of the film was 24mg, which was the difference in the weight of substrate between before and after deposition, and the thickness was about 11 μm . All chemicals used were reagent grade and deionized water was used.

RESULTS AND DISCUSSION

Digestion Several digestion technique of nitride have been reported[6-8]. Bollman[6] found that H_3PO_4 with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was a remarkable medium for dissolving nitrides. Passer et al.[7] employed alkali fusion to decompose nitride and to evolve ammonia. Using several acids and several alkali fluxes, ZrN was digested. A hundred mg of ZrN powder was completely decomposed in 5ml of 50% HF with 20ml of H_2O at 120-140°C for 10min, 5ml of 50% HF with 1 ml

of 30% H_2O_2 and 20ml of H_2O at 120–140°C for 10min, and 5ml of 50% HF with 5ml of 98% H_2SO_4 at 120–140°C for 80min. Although ZrN was digested in 10ml of 98% H_2SO_4 at 300°C for 60min, 10ml of 85% H_3PO_4 at 300°C for 30min, and 10 ml of 85% H_3PO_4 with 1.5g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ at 300°C for 30min, white precipitation appeared and it is difficult to transfer the material after the digestion with H_3PO_4 and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. Digestion with 10ml of 36% HCl at 150°C was not complete. Although alkali fusion with 5g of NaOH, 5g of KOH, 5g of Na_2CO_3 , 5g of K_2CO_3 and 5g of NaOH with 0.5g of B_2O_3 was tried, no flux completely decomposed 100mg of ZrN.

After the digestion of ZrN with HF, HF with H_2O_2 and HF with H_2SO_4 , nitrogen was determined by the titration method. The analytical results were 10.76–10.80%. Zirconium, carbon and oxygen were also determined with the ICP-AES instrument, a carbon/sulfur determinator (Leco corp. CS244) and a nitrogen/oxygen determinator (Leco Corp. TC36). The sum of the analytical results of the four elements, i.e., 87.51% for zirconium, 0.40% for carbon and 1.51% for oxygen, was 100.18–100.22%, which indicate that nitrogen completely changed into NH_3 without loss.

Titration The accuracy and the precision of the titration using the autotitrator was investigated in the following manner. After adding 1.7–85mg of $(\text{NH}_4)_2\text{CO}_3$, which correspond to 0.5–25mg of nitrogen, to 50ml of 0.025M H_2SO_4 , the solutions were heated at 100°C for 30min, followed by the titration with 0.05M NaOH. Maximum differentiating pH vs. volume of titrant was automatically observed as an end point. Five titrations were carried out for the solution of each concentration, and the average and the relative standard deviation (RSD) was calculated. As shown in Fig.1, the average of nitrogen concentration was constant and independent on the amount of nitrogen in the solution titrated, which indicate that even if the concentration of the solution is low, the same accuracy can be obtained as the one obtained by titrating the solution of higher concentration. The standard deviations of the volume of the titrant were almost constant (0.02–0.04ml), and so the RSD decreased from 4.2 to 0.15% in linear rate as the amount of nitrogen increased from 0.5 to 25mg. Taking account of back-titration, the titration is probably carried out by a skillful person with standard deviation of 0.05ml or more. As compared with it, the standard deviation obtained with the autotitrator was small. Assuming that 3/5 of the sample solution obtained by the digestion of ZrN film is used for the titration, 0.5–25mg of nitrogen correspond to 6.3–310mg of ZrN.

Fig.1. Dependence of RSD (O) and obtained concentration of nitrogen in $(\text{NH}_4)_2\text{CO}_3$ (□) on amount of nitrogen.

ICP-AES Yttrium was employed as an internal standard, and 343.823nm and 360.073nm were selected as spectral lines for zirconium and yttrium respectively, because the ionization energy of yttrium is close to that of zirconium and the excitation energy of the two

lines are almost the same. In order to find optimum operating conditions, the dependence of signal ratio of zirconium to yttrium on central gas flow rate was investigated, at various RF power and various observing height. Adjusting an observing height to 10mm, the dependence was small as shown in Fig.2. The plots in Fig.3 show the dependence of the correlation coefficient (r) between signal of zirconium and yttrium upon central gas flow rate at various RF power. An observing height was fixed at 10mm. In the range of 0.70 to 0.91 l/min, the r was almost constant. The dependence of the r on RF power was small. Hereinafter the observing height, the central gas flow rate and the RF power were adjusted to 10mm, 0.84 l/min and 1.2kW respectively.

Fig.2. Dependence of signal ratio on central gas flow rate at various RF power (1.0kW(O), 1.2kW(□) and 1.4kW(Δ)) and various observing height (5mm(A), 10mm(B) and 15mm(C)).

Fig.3. Dependence of correlation coefficient between signal of zirconium and yttrium on central gas flow rate at various RF power (1.0kW(O), 1.2kW(□) and 1.4kW(Δ)).

The solutions were prepared, containing 0-200mg/l Zr, 10mg/l Y, 12% HNO_3 , 0.5% HF and 0.5% H_3BO_3 . The calibration curve was computed from the relationship between the concentration and the internal standardized signal of zirconium in each solution. The signal of zirconium in each solution was measured again, and the concentrations of zirconium were calculated from the signals using the calibration curve. Repeating the procedure five times, the RSD of the concentrations obtained were calculated. In the range of 4 to 200mg/l, the RSD was less than 0.2%. Assuming that 1/10 of the sample solution is diluted to 100ml for the measurement, 4-200mg/l of zirconium correspond to 4.6-230mg of ZrN.

Thin film analysis Zirconium nitride film was digested in 10ml of 50% of HF at 120-140°C for 10 min and then the volume of the sample solution was adjusted to 50ml. After adding 5g of H_3BO_3 , 300ml of H_2O , 20ml of 50% NaOH into 30ml of the sample solution, NH_3 was distilled and collected in 50ml of 0.025M H_2SO_4 , followed by the determination of nitrogen by the titration with 0.05M NaOH. Zirconium, on the other hand, was determined by ICP-AES, after adding 10ml of 5% H_3BO_3 , 20ml of 60% HNO_3 and 10ml of 100mg/l Y solution into 5ml of the sample solution and adjusting the volume of the solution to 100ml. The obtained molar ratio of zirconium to nitrogen was 1:0.99 and the RSD for 4 samples was 0.49%. The weight of the deposition was coincident with the sum of the amount of zirconium and nitrogen obtained in this work, and carbon and oxygen were not detected by AES (JEOL Ltd. JAMP-7100) except the outer 2nm, which indicate that the analytical results were accurate.

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