togr. Library Vol. 31, Elsevier Science Publishers B. V., 131-134 (1985).
8. A. E. Martell, "Stability constants of metal-ion complexes", part II, The chemical society, 318-320, 539-540 (1971).
9. P. R. Haddad and R. C. Foley, J. of chromatogr., 500, 301 (1990).
10. D. D. Perrin, "Stability constants of metal-ion complexes", part B, organic ligands, IUPAC chemical data series-No. 22, 171-180, 557-558 (1983).

Determination of Trace Impurities in Gold by Isotope Dilution Inductively Coupled Plasma Mass Spectrometry

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Gold bonding wire of 0.076 mm in diameter used in semiconductor industry, is dissoved in aqua regia. The solution is then evaporated to near dryness several times with a few drops of HCl added to prepare the final sample solution in 5% HCl. The gold matrix is separated from trace impurities by controlled potential deposition. The whole electrolysis has been carried out inside a clean bench. An optimum potential is found to be +0.25 V to give more than 99.9% Au matrix removal with better than 90 analytes remaining in the electrolyte solution. Isotope dilution calibration is employed to get the best accuracy and precision. Analytical results are presented with determination limits of the analytical method.

Introduction

Inductively Coupled Plasma-Mass Spectrometry(ICP-MS) is being widely applied to the various application areas of trace element and isotope ratio determinations.[1] In contrast to the many application areas such as geological, environmental and clinical fields, only a few papers have been published on metallurgical applications.[2-5] Recently, the demand of high-purity metals is increasing especially in electronics industry. Since ICP-MS offers isotope dilution capability as well as extremely low detection limits, the determination of ultra trace impurities in pure metals can be also one of the important applications areas of ICP-MS.

Gold bonding wire is an important material in the production of the integrated circuits, where a high level of quality control is required. Trace impurities of transition metals such as Fe, Ni, and Cr adversely affect voltage threshold and etching uniformity. Trace impurities of radioactive elements increase the susceptibility to alpha-particle induced damage (soft errors). Reduction of the soft errors requires gold wires of high purity with respect to the radioactive elements such as U and Th, and thus the impurities of U and Th in the gold bonding wire are required to be below 1 ng/g.

Although part-per-trillion (ppt) levels of trace impurities in solution can be detected by ICP-MS, the matrix separation is almost always required for accurate and precise determination of ultra-trace impurities in pure metals. Of the many separation methods available at the present time, the controlled potential deposition[6,7] has a few advantage such as simplicity and freedom from contamination. In this report, a new analytical method is introduced to determine trace impurities in gold wire of 0.076 mm in diameter. The gold matrix is removed from the sample solution by the controlled potential deposition prior to the isotope dilution analysis by ICP-MS.

Experimental

Reagents. The analytical-reagent grade mineral acids were purified using sub-boiling, quartz-distillator. All laboratory wares were washed with deionized water obtained from a Milli-Q system (Millipore, Bedford, MA, USA). The enriched stable isotopes were purchased from US Services (Summit, NJ, USA).

Instrumentation. The ICP-MS system used in this work was a laboratory-built unit and its schematic diagram was given in the previous work.[8] The typical ICP-MS operating conditions are listed in Table 1. Figure 1 shows the electrolysis cell configuration for the controlled potential electrodeposition. The cathode is made of platinum and is in a form of gauze cylinder 3 cm in diameter and 6 cm in length. The anode is made of platinum and is in a form of rod 4 mm in diameter. The saturated calomel electrode (SCE) is used as a reference electrode. A laboratory built potentiostat was used to control the applied potential and the electrolysis was performed inside a clean bench.

Sample Preparation. 0.5 g of gold wire is weighed into a 100 ml teflon beaker. Then 4 ml of aqua regia is added to dissolve the gold wire. The beaker is placed on a hot

Table 1. ICP-MS Operating Condition

Inductively Coupled Plasma	
Forward Power	1.0 kW
Reflected Power	<2 W
Coolant Flow Rate	12 L/min
Auxiliary Flow Rate	0.5 L/min
Carrier Gas Flow Rate	0.5 L/min
Sample Uptake Rate	0.8 mL/min
Sampling Depth	10 mm
Mass Spectrometer	
Interface Pressure	1.6 torr
Quadrupole Chamber Pressure	3×10^{-6} torr
Sampler	Aluminum, 1 mm oriffice
Skimmer	Aluminum, 0.7 mm orifice
Data Acquisition	
Measurement Mode	Multichannel Scanning
Channel Dwell Time	5 ms
Average Number of Channels per amu	13.7
Integration per Channel	1 s

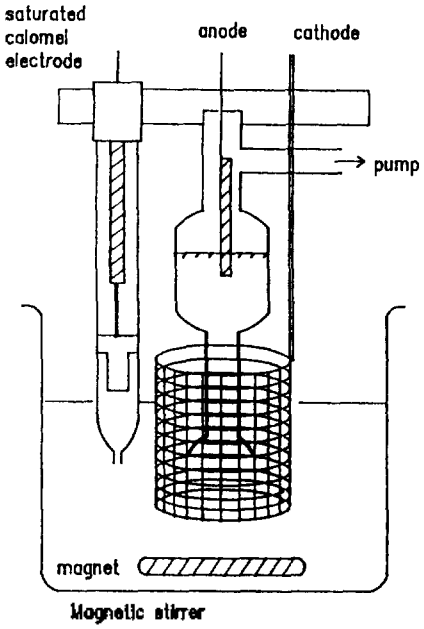

Figure 1. Three electrodes for controlled potential electrodeposition.

plate until incipient dryness. 2 ml of HCl is added and above steps are repeated four times. Final solution for the electrolysis is prepared by adding 50 ml of 5% HCl solution with known amounts of spike isotopes.

Electrolytic Deposition Procedure. Bottom end of the anode is about 5 cm above the solution surface and the anode is placed inside a pyrex tubing as shown in figure 1. The pyrex tubing is pumped by an air pump (Foxboro Analytical, USA) so that the chlorine gas evolved during the electrolysis can be effciently removed. The pumping also raises the level of the sample solution inside the pyrex tubing for an electrical contact between the anode and cathode.

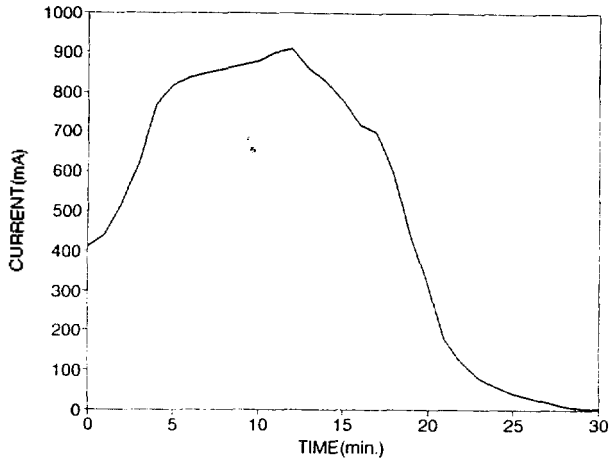

Figure 2. Chronoamperogram of 0.912% Au in 5% HCl at +0.25 V *vs.* SCE.

Table 2. Separation of Au Matrix by C.P.E

Applied Potential (vs SCE)	Au matrix in Solution (ppm)	Au Separation Efficiency (%)	Electrodeposition Time (Min)
+0.05	2.53	99.75	20
+0.10	3.94	99.61	14
+0.15	4.15	99.58	16
+0.20	1.71	99.83	17
+0.25	3.93	99.61	18

0.1% Au in 10% HCl.

The solution is stirred at about 1000 rpm with a magnetic stirrer (Fisher Scientific, USA) for an efficient electrodeposition. The electrolysis is stopped when the current flowing in the cell does not decrease as shown in the chronoamperogram Figure 2.

Results and Discussion

Optimization of Electrolytic Deposition. In an ideal matrix separation method, the matrix separation efficiency should be close to 100% without losing analytes. In real situations, however, the higher efficiency generally means the more analytes loss. For the matrix separation by the controlled potential deposition, the important parameters to be optimized are the applied potential, acidity of solution, and the required deposition time. In order to optimize the applied potential, the Au separation efficiency was investigated by varying the potential from 0 V to+0.2 V. The 0.1% Au standard solution in 10% HCl was prepared for this purpose. As shown in Table 2, the Au separation efficiency is found to be more than 99.58% for all applied postentials used in this experiment. And the deposition time required for complete reaction is less than 20 min.

In order to examine the recovery efficiencies for Cu, Fe, Pt, Th, U, and Pd during electrodeposition, the 10 ppm standard solution of each element was added to the 0.1% standard Au solution. Affter electrodeposition, the residue solution was introduced into ICP-AES to determine the concentrations of the six analytes. Table 3 shows the recovery

Table 3. Recovery Efficiency of Analytes

Applied Potential (*vs.* SCE)	Recovery Efficiency of Spiked Elements (%)				
	Cu	Fe	Pt	Th	Pd
+0.05	73.5	90.3	81.2	82.3	53.5
+0.10	87.1	91.8	83.7	82.6	63.8
+0.15	88.2	88.7	85.3	80.2	52.4
+0.20	95.4	92.2	85.2	83.6	100.4
+0.25	96.1	92.3	85.0	84.2	92.2

10% HCl 용액.

Table 4. Reproducibility of Analyte Recovery Efficiency (+0.25 V *vs.* SCE)

Electrolyte		Recovery Efficiency (%)					
		Cu	Fe	Pt	Th	U	Pd
5% HCl	Average	91.9	93.3	90.0	93.7	90.4	89.3
	± SD	± 1.6	± 1.2	± 1.2	± 1.7	± 2.9	± 1.4
	RSD (%)	1.8	1.3	1.4	1.8	3.2	1.6
10% HCl	Average	90.4	89.2	85.2	87.6	88.7	88.0
	± SD	± 1.3	± 2.8	± 1.5	± 3.4	± 1.5	± 0.3
	RSD (%)	2.9	3.1	1.7	3.8	2.3	0.4

* RSD values based on four measurements.

Table 5. Two Isotopes Selected for Isotope Dilution

Isotope	Abundance (%)	
	Natural	Spike
^{60}Ni	26.4	1.13
^{62}Ni	3.71	97.01
^{63}Cu	69.1	0.3
^{65}Cu	30.9	99.7
^{64}Zn	48.6	0.95
^{68}Zn	18.8	97.9
^{107}Ag	51.8	0.5
^{109}Ag	48.2	99.5
^{206}Pb	24.1	92.15
^{208}Pb	52.4	1.25

efficiencies of six analytes as the applied potential is varied from 0.05 to 0.25 V. In Table 4 are listed the recovery efficiencies of six analytes for five measurements at an applied potential of +0.25% V. The reproducibility of the analyte recovery efficiency is found to be less than 3.2% in 5% HCl solution. Also the effect of electrolyte acidity on the recovery efficiency is shown in Table 4.

The optimum experimental condition was found to be at +0.25 V of cathode. However, such an analyte loss does not give any error in Ag quantification by isotope dilution method because the two Ag isotopes are removed at the same rate and hence the Ag isotope ratio does not change. The peaks at 104, 105, 106, 108, and 110 are those of Pd isotopes. Figure 6 shows isotope dilution mass spectrum of Pd in gold sample solution. Solid line peak was obtained by spiking 0.22 μg of ^{206}Pb to 0.5 g gold sample and dotted line peak by spiking 0.11 μg of ^{206}Pb to blank solution.

Table 6. Analytical results of NIST SRM 685

Element	Determined Concentration (μg/g)	Best Range of NIST (μg/g)
Mg	0.062± 0.006	<0.2
Cu	0.098± 0.020	<0.1-0.26

Table 7. Analytical results of Au bonding wire (heavy metals)

Sample I.D.	Determined Concenration (μg/g)				
	Ni	Cu	Zn	Ag	Pd
Blank	0.35	0.06	0.07	0.53	0.05
Sample #1	0.06	–	0.05	–	0.16
Sample #2	0.09	0.46	0.01	–	0.18
Sample #3	0.05	0.39	0.07	3.22	0.19
Sample #4	0.10	0.50	0.02	3.26	0.21
Sample #5	0.06	0.48	0.11	2.87	0.19
Mean± SD	0.07± 0.02	0.45± 0.05	0.05± 0.05	3.11± 0.21	0.18± 0.02
RSD (%)	30.1	10.5	77.4	6.9	9.7
Best Range	<0.10	0.45± 0.05	<0.11	3.11± 0.3	0.18± 0.02

Table 8. Analytical results of Au bonding wire (radioactive elements)

Sample I.D.	Element	
	Th*	U*
Blank 1	463± 53	295± 31
Blank 2	376± 32	319± 23
1 ppb Standard	5139± 142	5020± 110
Sample #1	797± 29	319± 22
Sample #2	770± 88	328± 18
Sample #3	850± 15	317± 35
Best Range	<8.5 ng/g	<1.9 ng/g

* 5 channel integrated counts.

Analytical Result. High-purity gold standard reference material (NIST SRM 685) was analyzed to control accuracy of the developed analytical method. In Table 6 are listed determined concentrations of Mg and Cu together with the certified values provided by the NIST. It can be seen that the determined concentrations are well within the best ranges given by the NIST.

Table 7 shows the analyzed values of trace impurities of Ni, Cu, Zn, Ag, and Pd in gold bonding wire. The values in Table 7 are averages of five measurements from five different spools of gold wire. In Table 7, the RSD values of Ni and Zn are considerably higher than those of other elements, which is not caused by inhomogeneity, but by poor analytical reproducibility due to low concentrations. The poor reproducibility and high background signal are mainly due to the blank contamination. This kind of blank contamination is originated from the impurities of the acid, the electrodes, and the apparatus used in the electrodeposition. Definitely,

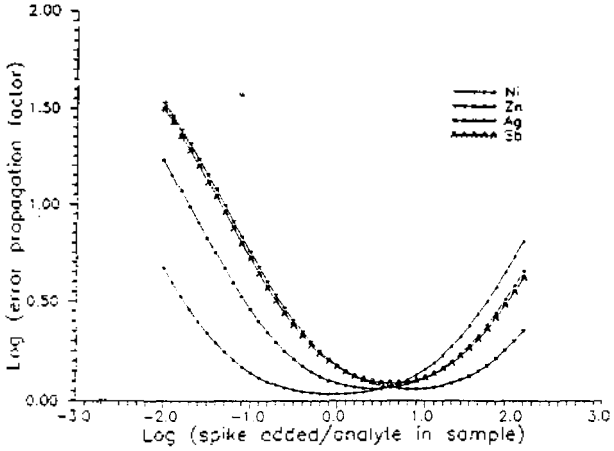

Figure 3. Error propagation of isotope dilution (for 15% error in isotope ratio measurement).

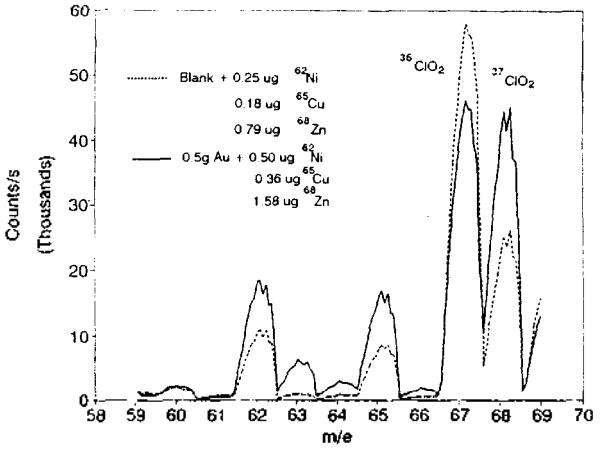

Figure 4. Isotope dilution mass spetrum of Ni, Cu, and Zn in 1% Au sample solution.

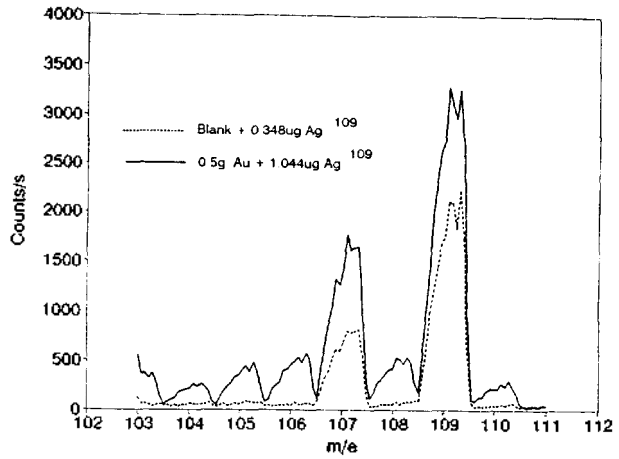

Figure 5. Isotope dilution mass spetrum of Ag in 1% Au sample solution.

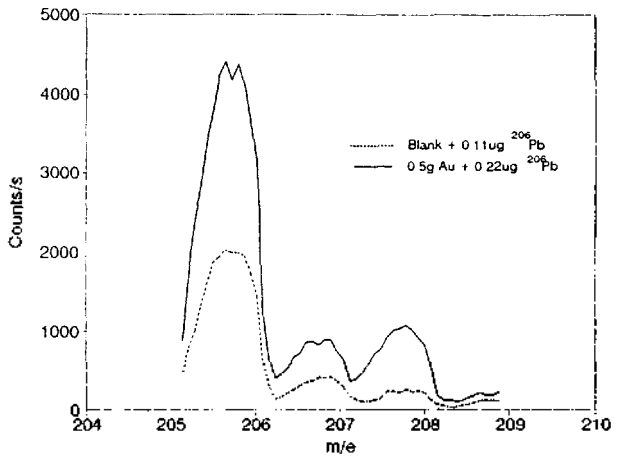

Figure 6. Isotope dilution mass spetrum of Pb in 1% Au sample solution.

the quality control to minimize the blank contamination has to be performed.

In the case of Cu, Ag, and Pb which have relatively high concentrations, RSD values are less than 10%. In Figure 7, are illustrated mass spectra of Th and U. The peaks drawn by solid line, large dotted line, and small dotted line were obtained from 1 ppb standard solution, gold wire sample and blank respectively. In Table 8, are listed.

Isotope Dilution The isotope dilution method is especially useful when a sample has to undergo some chemical pretreatment before analysis, because any analyte loss during the pretreament does not affect the final results.[9] Listed in Table 5 are two isotopes of each analyte for the isotope dilution analysis and the enrichment of the spike isotopes. Figure 3 illustrates the relationship between the error propagation[10] for 1% error in the mixture isotope ratio and the ratio of the spike isotope amount to the analyte amount in the sample. Figure 3 shows that the optimum spike isotope amount is slightly different for each analyte and that the optimum is observed between one and ten times the analyte amount originally in the sample. The amounts of the spike isotopes added to the blank and sample were determined on the basis of the error propagation as shown in Figure 3. Figure 4 shows isotope dilution mass spectrum of Ni, Cu, and Zn analytes(solid line) measured from the gold sample solution spiked with 0.5 μg of ^{62}Ni, 0.36 μg of ^{65}Cu, and 1.58 μg of ^{68}Zn. In Figure 4, dotted line indicates the spectrum of blank solution which went through the same process of the sample preparation after spiking half as much as the amount of spike isotope to gold sample. As shown in Figure 4, there is not much difference between blank and sample peaks at 60 of m/e. Therefore, it is considered that the amount of the Ni impurities in the gold sample is close to the detection limit. This the reason why the RSD for the Ni in Table 7 is not good. However, the Cu and Zn impurities can be quantified from the mass spectrum. Figure 5 shows isotope dilution mass spectrum of Ag analyte. As in Figure 4, solid line peak was obtained by spiking 1.044 μg of ^{109}Ag to 0.5 g gold sample and dotted line peak by spiking 0.348 μg of ^{109}Ag to blank solution. In Figure 5, the ratio of solid line ^{109}Ag peak to dotted line ^{109}Ag peak does not agree with the amounts of ^{109}Ag spiking to the two solutions. This is because considerable amount of Ag was removed by deposition onto the platinum cathode. However, such an analyte loss does not give any error in Ag standard solutions

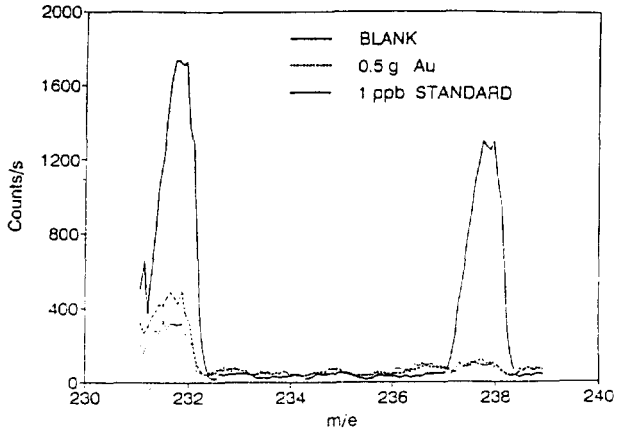

Figure 7. ICP mass spetrum of Th and U.

and three gold wire samples, together with the best ranges detemined with the integrated counts.

Conclusion

A new analytical method has been successfully employed for pure gold samples. The analytical method takes advantage of the clean and simple matrix separation technique of the controlled potential deposition followed by the highly accurate and precise isotope dilution mass spetrometry. However, the blank contamination has to be minimized in order to get more precise results. Sensitivity enhancement was found necessary to improve precision and accuracy for ultra-trace elements (Ni, Zn, Th and U). Thus more efficient sample introduction methods such as ultrasonic nebulizer and electrothermal vaporizer could give better results.

References

1. J. W. Mclaren, *ICP In formation Newsletter*, **16**, 371 (1990).
2. C. W. Mcleod *et al.*, *Spectrochim. Acta*, **41B**, 169 (1986).
3. H. P. Longerich, B. J. Fryer, and D. F. Strong, *Spectrochim, Acta*, **42B**, 101 (1987).
4. A. makishima, I. Inamoto, and K. Chiba, *Appl. Spectrosc.*, **44**, 91 (1990).
5. S. K. Luo and F. C. Chang, *Spectrochim. Acta*, **45B**, 527 (1990).
6. B. H. Vassons, R. F. Hirsch, and H. Letterman, *Anal. Chem.*, **45**, 793 (1973).
7. J. Shiowatana and J. P. Matousek, *Talanta*, **38**, 375 (1991).
8. C. J. Park and K. W. Lee, *Anal. Sci. and Tech.*, **3**, 381 (1990).
9. A. A. Van Heuzen, T. Hoekstra, and B. Van Wingerden, *J. Anal. At Spectrom.*, **4**, 483 (1989).
10. C. J. Park and K. W. Lee, *Anal. Sci. and Tech.*, **3**, 25 (1990).

Effects of Heat Treatment and Platinum Loading on CdS Particles in the Photocatalytic Alanine Synthesis

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The photocatalytic alanine and hydrogen production reaction were studied by using CdS as a semiconductor photocatalysts. The rate of alanine and hydrogen production depends strongly on the temperature in heat treatment of CdS powder. In particular, the rate of alanine production, which was observed using Pt/CdS(A)-(CdS from Mitsuwa), was increased about six times than that of using Pt/CdS(B)-(CdS from Furruchi) under the same heat treatment condition at 500℃. And the photocatalytic activity for alanine production using bare CdS(A) or Pt/CdS(A) was almost same with increasing temperature in heat treatment in the range of 100-600℃. From X-ray diffraction data and photoluminescence spectrum, we conclude that the crystal structure changes of CdS(A) or strong interaction at interface of Pt and CdS contribute to increasing the rate of alanine and hydrogen production reaction.

Introduction

The control of photocatalytic organic reactions is one of the very interesting subjects. Bard *et al.*[1] have examined that amino acid including alanine can be formed from methane-ammonia water in aqueous solution with Pt/TiO_2 as photocatalyst under near UV irradiation.

Sakada[2,3] have reported that various amino acids such as alanine were produced efficiently with visible light from ketocaboxylic acids in ammonia water through photocatalytic reaction with dyes, for example, zinc tetraphenylphosphine *p*-tetrasulfonate, acridine yellow and fluorescein derivatives, etc.

In the previous result[3], It was found that the photocatalytic