Determination of Trace Elements of Ge and P in a Gold Bonding Wire by Inductively Coupled Plasma Atomic Emission Spectrometry

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Inductively coupled plasma atomic emission spectrometry (ICP-AES) was used to determine the presence of germanium and phosphorus in a pure gold bonding wire. The samples were dissolved with hydrobromic acid and nitric acid at room temperature. The quantitation limits were 0.012 mg L^{-1} at 265.118 nm for Ge and 0.009 mg L^{-1} at 177.495 nm for P. Using the mixed acid digestion formula of DIW + HBr + HNO_3, the recoveries were in the range of 98-100% and the relative standard deviation was within 1.1-2.3%. On the other hand, the amount of Ge decreased by about 16.2% using DIW + HCl + HNO_3, due to the formation of a volatile compound. The Ge contents determined using the external method and the standard addition method were 9.45 mg kg^{-1} and 9.24 mg kg^{-1}, respectively, and the P contents, using the same methods, were 22.49 mg kg^{-1} and 23.09 mg kg^{-1}, respectively. Both methods were successfully used to determine the trace amounts of P and Ge in the pure gold bonding wire samples.

Key Words : ICP-AES, Gold, Trace, Ge, P

Introduction

Electrical interconnection is established between a semiconductor chip and a lead frame during the wire-bonding process.[1] Gold, which consists mainly of nanocrystalline, is used as a material for wire bonding because it is inert and has excellent loop formation capability and cyclic performance. In addition, the size of semiconductor packages is steadily being reduced, and the diameter of commercial ultra-fine gold wires has been decreased to 24 μm. With the decrease in the diameter of ultra-fine gold wires, their loading capacity and stiffness also decreased.[2,3] Moreover, with the decrease in semiconductor packages' pad pitch, the mechanical properties of gold bonding wires, which are thinner and harder, must be improved. The mechanical properties of gold bonding wires depend on the amount and type of their dopant (e.g., Be, Mg, Al, Si, P, Ca, Cu, Zn, Ge, Y, Pd, and La), which must have a purity of 99.99% to 99.999% to be included in a gold wire. Dopants affect the mechanical properties of gold wires due to the differences in the arrangement and sizes of the elements in the microstructure of polycrystalline gold.[4-6]

The measurement of the amount of dopants present in gold bonding wires, and of the dopants' trace impurities (which must be less than 0.01%), plays a critical role in quality control. Several spectral, matrix and molecular ion interference have been reported for ICP-MS analysis of gold, so determination limits achieved are around 1 ug g^{-1} for all studied analytes.[7] The determination of phosphorus by ICP-MS is still a challenging task: all the elements mentioned show high first ionization potentials and low ionization efficiency in an argon based plasma. Due to the formation of molecular ions such as $^{14}N^{16}O^{1}H^{+}$ inside the argon plasma, the detection of phosphorus is significantly disturbed.[8] ICP-AES has been succesfully applied for trace element determination in high purity gold.[9-11] but this method is not always available in routine laboratories. To measure the amount of Ge and P present in gold, the gold sample must be dissolved in *aqua regia* during the pretreatment process. In the presence of chloride matrix, loss of germanium caused by the formation of volatile $GeCl_4$ (m.p. −49.5 °C, b.p. 86.6 °C, Ge-Cl bond dissociation energy 431 KJ mol^{-1}) can occur.[12] Thus, its precise measurement cannot be ensured due to the volatilization of Ge.

The purpose of this study is to look into the possibility of improving the pretreatment method, the wavelength selection (line selection),[13] and the multi-simplex optimization.[14,15] As well as to compare the external and standard addition methods of matrix effect and uncertainty.[16] It measuring the amount of Ge and P in gold, using ICP-AES.

Experimental Procedure

Samples and Reagents. The bonding wire that was used in the semiconductor was a gold sample (MK electron Co. LTD, Yongin, Korea). The gold bonding wire used in this study contained a certain amount (several tens of mg kg^{-1}) of the dopants Ge and P.

Water used in these experiments was distilled and deionized by Nanopure system (Barnstead, Dubuque, IW, USA). HNO_3, HCl (DongWoo Chemicals, Seoul, Korea), HBr (Aldrich, Milwauke, WI, USA) were used for the preparation of samples and standard. Calibration solutions germanium and phosphorus were prepared from 10,000 mg kg^{-1} of single stock solution (SRM 3120a, SRM 3139a, NIST, Gaithersburg, MD, USA). To ensure matrix matching, each calibration solution also contained an appropriate amount of dissolved Au, high purity gold (SRM 685, NIST,

Gaithersburg. MD. USA).

Digestion Procedure. Gold is generally known to dissolve easily in *aqua regia*. When the Ge and Cl in gold are coupled. however. their products have a low boiling point (86.6 °C for $GeCl_4$, 28 °C for $GeHCl_3$, −20.6 °C for GeF_3Cl. and −2.8 °C for GeF_3Cl), which makes it difficult for them to be analyzed with precision due to the volatilization of Ge when HCl is used. For this reason, HBr was used instead of HCl for the pretreatment of the gold sample in this study. For the pretreatment. about 1 g of gold was taken and placed in a PFA vessel. and 2 mL of DIW, 6 mL of HBr. and 4 mL of HNO_3 were added to it. They were left to dissolve for 24 hrs at room temperature and were used to fill a 50 mL volumetric flask after it was confirmed that the gold sample had dissolved completely.

Instrumentation and Multi-simplex Optimization. The analytical measurements were carried out in an iCAP 6500 ICP-AES (ThermoElemental Ltd., UK) apparatus equipped with a PFA nebulizer. a teflon cyclonic chamber. and a peristaltic sample delivery pump. In the ICP-AES optimization. the nebulizer gas flow rate and the pump flow rate were the most important parameters among the operation parameters that determined intensity and precision. In the optimization that was done in this study, the one-factor-at-a-time method was used to obtain a satisfactory condition for the analysis. It took this method a long time, however, not only to find the optimization condition but also to determine whether or not an optimization condition better than the one that was found existed. To avoid these drawbacks, the multi-simplex method was used in this study for optimization purposes. Multi-simplex is a method of finding the optimization condition with the least attempts by reflecting, expanding. and contracting the K+1 geometrical figure in a K-dimensional space (K is a parameter's number). It takes less time for the multi-simplex method to find the optimization condition. and there is a higher possibility that it could find the best optimization condition. Figure 1 shows the results of the 10-time measurement of Mn (1 mg L^{-1}) using the multi-simplex method. The best intensity (95.270) and the best % RSD (0.344) were obtained at the 0.66 L min^{-1} nebulizer gas flow rate and at the 49rpm pump flow rate. The instrument settings and data acquisition parameters that were used are summarized in Table 1. For signal stabilization, a sample read delay of 75 secs was chosen. In between the loading of the solutions of both the samples and the standards, the sampling system was rinsed with 5% HNO_3 for 75 secs.

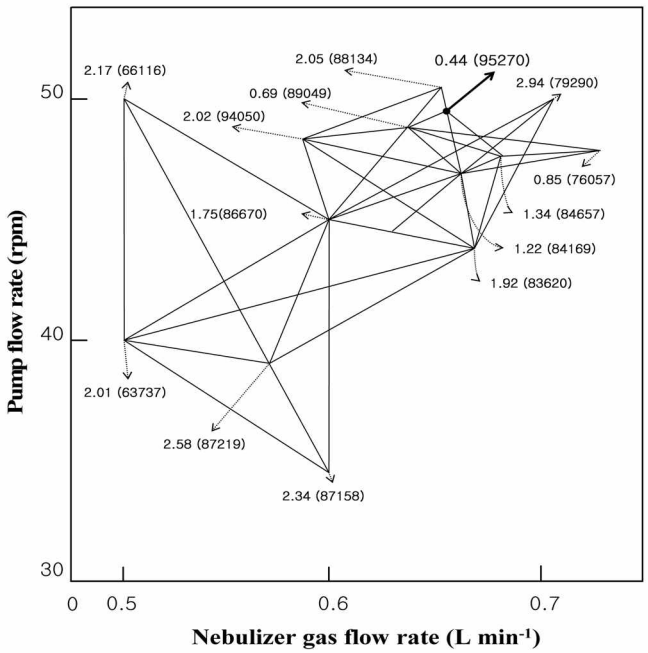

Figure 1. Optimization conditions of pump flow rate and nebulizer flow rate by multi-simplex method.

Table 1. Operating Conditions and Data Acquisition Parameters of ICP-AES

Rf power (W)	1150
Sample uptake rate (rpm)	49
Cooling gas flow rate (L min^{-1})	12
Auxiliary gas flow rate (L min^{-1})	0.5
Nebulizer gas flow rate (L min^{-1})	0.66
View	Axial
Nebulizer	PFA nebulizer
Spray chamber	Teflon cyclonic chamber

Results and Discussion

Line Selection. The spectral interference was investigated at wavelengths of 187.426 nm, 206.866 nm. 209.426 nm, 219.871 nm, 265.118 nm. and 265.158 nm for germanium, and 177.495 nm, 178.284 nm, 178.766 nm, 185.891 nm, 185.942 nm, 213.618 nm. and 214.918 nm for phosphorus. After a two-point background correction was made, no spectral interference was found at all the wavelengths for Ge. and a spectral interference was found only at 178.234 nm and 178.322 nm for P (178.322 nm is a wavelength of the spectral interference for Au). In addition, the LOD (limit

Table 2. Line Selection, Limits of Detection (LOD), and Limits of Quantitation (LOQ) for the ICP-AES Determination of Ge and P Elements in Gold Bonding wire

Element	Wavelength (nm)	LOD (mg L^{-1})	LOQ (mg L^{-1})
Ge	187.426	0.076	0.254
	206.866	0.004	0.014
	209.426	0.003	0.013
	219.871	0.004	0.014
	265.118	0.004	0.012
	265.158	0.015	0.049
P	177.495	0.003	0.009
	178.284	0.004	0.014
	178.766	0.004	0.014
	185.891	0.024	0.079
	185.942	0.011	0.038
	213.618	0.005	0.017
	214.914	0.005	0.017

of detection) and LOQ (limit of quantitation) were obtained using ICP-AES to determine the analyzability of the gold sample, because its Ge and P contents were low. As shown in Table 2, the wavelength with the best LOQ was 0.012 mg L^{-1} at 265.118 nm for Ge, and 0.009 mg L^{-1} at 177.495 nm for P. Thus, in this study, Ge and P were analyzed using these two wavelengths.

Recovery Test and Dilution Factor. As there is no reference material that states that Ge and P are present in gold, two experiments were used to conduct a recovery test for Ge and P, using the acid digestion method. In the first experiment, DIW + HBr + HNO_3 (2 mL, 6 mL and 4 mL) and DIW + HCl + HNO_3 (2 mL, 6 mL and 4 mL), without gold, were placed in PFA vessels, and 1 mL each of Ge (500 mg L^{-1}) and P (500 mg L^{-1}) standard solutions were added to these. They were left to dissolve for 24 hrs at room temperature, were used to fill a 50 mL volumetric flask, and were diluted at a 1:10 ratio for analysis purposes. In the second experiment, 1 g of gold (pure gold standard NIST SRM 685) was placed in PFA vessels, and Ge and P standard solutions and acids were added to these, as in the first experiment, for the recovery test. As shown in Figure 2, the detected amounts of Ge and P were identical, regardless of the type of acid, when the experiment was conducted without gold. On the other hand, the detected amounts of P were identical, regardless of the type of acid, but the amount of Ge detected in DIW + HCl + HNO_3 was about 16.2% less than that detected in DIW + HBr + HNO_3, when the experiment was conducted with gold. Also, the results of the pretreatment in the above two acid digestion methods with the pure gold standard NIST SRM 685, were analyzed and were all found to have been below the detection limit.

The best wavelengths for Ge and P in ICP-AES were 265.118 nm and 177.495 nm, respectively, and their limits of quantitation were 0.012 mg L^{-1} and 0.009 mg L^{-1}, respectively. In addition, the amounts of Ge and P that were expected to be present in the gold sample were several tens of mg kg^{-1}. Therefore, 1 g of the gold sample was taken, and

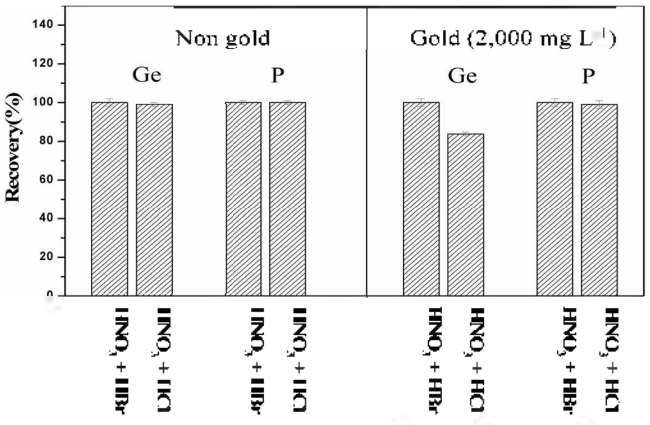

Figure 2. Ge and P recovery test depending on kinds of acid and the gold matrix effect. Each bar indicates the average recovery rate (%) of three measurements after three sample treatments, and the straight lines show the standard deviation. The amount of Ge and P that was added was 1 mg L^{-1} each.

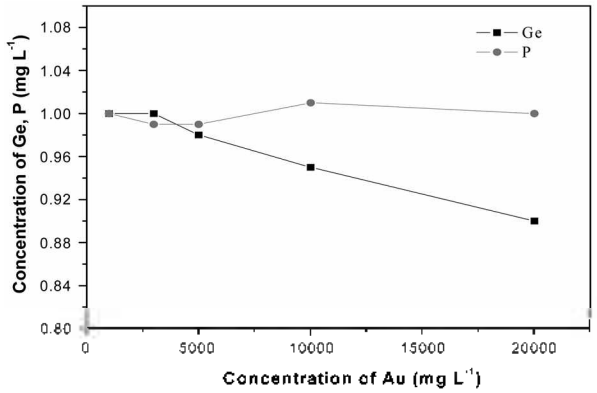

Figure 3. The matrix effect of Ge and P depending on the gold concentrations.

DIW + HBr + HNO_3 (2 mL, 6 mL and 4 mL) was added to it for acid digestion. Then this solution was used to fill a 50 mL volumetric flask and was diluted at a 1:10 ratio by assuming that the Ge and P contents of the gold sample were both 10 mg kg^{-1}, which was the minimum. Based on the results of the analysis, the amount of Ge and P that was present in the gold sample was 0.02 mg kg^{-1} or more. Therefore, their dilution factor is thought to be proper.

Matrix Effect and Robustness Test. 1.000 mg L^{-1}, 3.000 mg L^{-1}, 5.000 mg L^{-1}, 10.000 mg L^{-1}, and 20,000 mg L^{-1} of gold (pure gold standard NIST SRM 685) were taken and standard solutions of Ge and P were spiked to yield a concentration of 1 mg L^{-1} for analysis purposes. As shown in Figure 3, Ge decreased in the 3,000 mg L^{-1} gold concentration, whereas P was not affected by the gold concentration. Therefore, it was found that the dilution factor (1/500) that was used earlier, which was selected so as to come up with a 2,000 mg L^{-1} gold concentration, was not affected by the matrix effect. Furthermore, the Mg standard solution was spiked in 2,000 mg L^{-1} gold (pure gold standard NIST SRM 685) to yield a concentration of 1 mg L^{-1}, which was used to identify the influence of the operating conditions on the Mg (II)/Mg (I) line intensity ratio. The 280 nm Mg (II)/285 nm Mg (I) line intensity ratio was measured to evaluate the robustness of the plasma. To compensate for the different wavelength responses of the dispersive system at 280 and 285 nm, the experimental ratio was multiplied by 1.8. The factor 1.8 was obtained by introducing water and measuring the background at the two wavelengths, assuming that the continuum was flat between 280 and 285 nm. The equation MgII (280 nm)/MgI (285 nm) × B285/B280 (1.8) 10 must be satisfied, in general. The value obtained in this study was 12.95. As such, the above equation was satisfied for the analysis of Ge and P in 2,000 mg L^{-1} gold.

Evaluation of the Uncertainty of the External and Standard Addition Methods. The gold samples were treated with DIW + HBr + HNO_3 (2 mL, 6 mL and 4 mL) and were used to fill a 50 mL volumetric flask for the sample solution. The sample solution was analyzed and evaluated using the external and standard addition methods. In the external method, the above sample solution was diluted at a

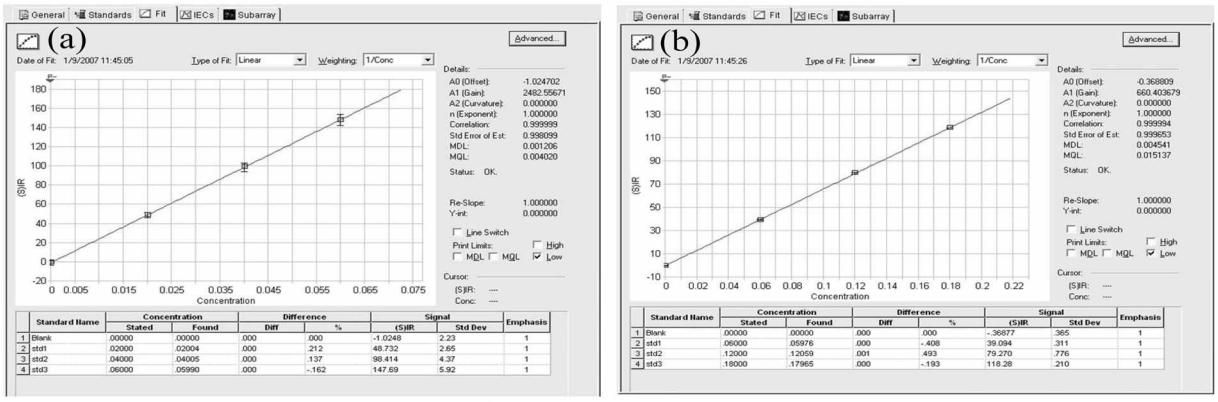

Figure 4. Calibration curves using the external method for (a) Ge and (b) P.

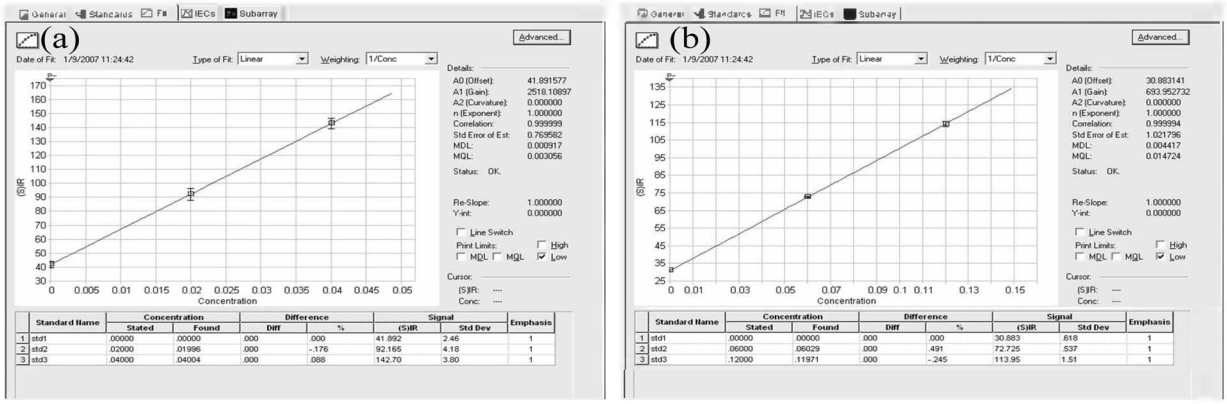

Figure 5. Calibration curves using the standard addition method for (a) Ge and (b) P.

1:10 ratio, and calibration curves were prepared, as shown in Figures 4(a) and 4(b), for the analysis of Ge and P. In the standard addition method, the above sample solution was diluted at a 1:10 ratio using three volumetric flasks, and was spiked to yield Ge concentrations of 0 mg L^{-1}, 0.02 mg L^{-1} and 0.04 mg L^{-1}, and P concentrations of 0 mg L^{-1}, 0.06 mg L^{-1} and 0.12 mg L^{-1} for analysis purposes, as shown in Figures 5(a) and 5(b). Table 3 shows the results and levels of uncertainties of the comparison and analysis of Ge and P. First, with respect to the level of uncertainty of both methods, the uncertainty was more significant in the external method than in the standard method. This is because the same uncertainty factors were applied to both methods, until the sample digestion step, which led to the same level of uncertainty, and because the uncertainty factors differed in the preparation of calibration curves, which led to the different levels of uncertainty of the two methods. The uncertainty equation for the external method's calibration curve is Equation 1, and that for the standard addition method's calibration curve is Equation 2. The 1/p factor is included in Equation 1 and is not included in Equation 2, which leads to a more significant uncertainty with respect to the external method than in the standard method, wherein p is the number of times measurement was done to determine c_0.

$$u(c_0) = \frac{s}{B_1}\sqrt{\frac{1}{p} + \frac{1}{n} \times \frac{(c_0 - \bar{c})^2}{S_{xx}}} \quad (1)$$

$$u(c_0) = \frac{s}{B_1}\sqrt{\frac{1}{n} \times \frac{(c_0 - \bar{c})^2}{S_{xx}}} \quad (2)$$

Furthermore, as shown in Table 3, the Ge content was 9.45 mg kg^{-1} and 9.24 mg kg^{-1}, when the external method and the standard addition method were used, respectively, which shows an approximately 2.3% difference. The P content was 22.49 mg kg^{-1} and 23.09 mg kg^{-1} for the same methods, respectively, which shows an approximately 2.6% difference. Based on these results, no difference was found between the two methods in terms of their uncertainty factor. This shows that the matrix effect has no effect on a 3.000 mg L^{-1} gold concentration, as shown Figure 3.

In this study, several tens of mg kg^{-1} of Ge and P that were present in gold were successfully analyzed using the external and standard addition methods. The results of the analysis

Table 3. Results and Uncertainties Obtained Using the Standard Addition Method and External Method

Gold sample	Standard addition		External	
	Ge (mg kg^{-1})	P (mg kg^{-1})	Ge (mg kg^{-1})	P (mg kg^{-1})
Result[a]	9.45	22.49	9.24	23.09
Uncertainty[b]	0.93	2.23	1.39	2.37

[a]Results are the average of three samples (replicate 3). [b]95% confidence interval.

show that both methods can be effectively used to determine the amount of Ge and P present in gold. It is thought, however, that the standard addition method has an edge over the external method, particularly when considering uncertainty, as it is capable of obtaining analysis results with a considerably smaller range of uncertainty.

Conclusions

Open-system digestion using hydrobromic acid (HBr) and nitric acid (HNO_3) was proven to allow satisfactory determination of traces of Ge and P in a pure gold bonding wire using ICP-AES. The formation of volatile compounds such as $GeCl_4$ was significantly reduced. The results of both methods show an approximately 2.3% difference in Ge and 2.6% difference in P. These results were found the small amount of difference between the two methods in terms of their physical effect by total dissolved solids below in 2,000 mg L^{-1} gold. The uncertainty of standard addition method compared with the external method was obtained about Ge 33.1% and P 5.9% less than that of the external method. From the results, we can understand that the standard addition method is a relatively more exact than that of the external method.

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