



CCQM-P98

Improvement of Quantitative Analysis of Fe-Ni Alloy Films Using a Certified Alloy Reference Film

**A pilot study for the Consultative Committee on Amount of
Substance**

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Improvement of Quantitative Analysis of Fe-Ni Alloy Films Using a Certified Alloy Reference Film

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A pilot study for the quantitative surface analysis of alloy films has been performed by the Surface Analysis Working Group of the Consultative Committee for Amount of Substance (CCQM). The aim of this pilot study is to ensure the equivalency in the measurement capability of national metrology institutes for the quantification of alloy films. The majority of the participants used x-ray photoelectron spectroscopy and Auger electron spectroscopy which are useful methods for the quantitative analysis of thin alloy films or structured surfaces made of them. The compositions of the test samples were certified by inductively coupled plasma mass spectrometry with isotope dilution method. The in-depth and lateral homogeneities of the composition were confirmed by secondary ion mass spectrometry using C₆₀ ion source. In this pilot study, the quantification of Fe-Ni alloy films was found to be a good candidate as a subject for CCQM key comparison. Linear fitting of the quantification results showed a great improvement in the equivalency of the offset value and uncertainty by the relative sensitivity factor determined from a Fe51-Ni49 alloy reference film rather than pure metal films.

1. INTRODUCTION

Pilot study and international key comparison of surface analysis have been launched by the Surface Analysis Working Group (SAWG) of the Consultative Committee for Amount of Substance (CCQM) in 2004. [1,2] The aim of the pilot study and key comparison is to ensure the equivalency in the measurement of National Metrology Institutes (NMIs). The first pilot study

(P-38) and key comparison (K-32) of SAWG were performed for the measurements of the thickness of ultra-thin SiO₂ thin films on Si(100) and Si(111) substrates. [3]

Quantitative surface analysis is one of the most important applications of surface analysis techniques. Although XPS and AES are generally used for the surface compositional analysis of multi-component alloy systems, accurate surface composition analysis is difficult due to matrix effect. The relative sensitivity factors (RSFs) determined from pure metals are generally applied for the quantification of alloy materials. However, the matrix effect due to atomic density, attenuation lengths of electrons and electron backscattering factor in the matrix materials should be taken into account. [4]

A calibration method using alloy reference materials is recommended for the quantitative analysis of binary alloys to compensate the matrix effect. The best method for the quantification of binary alloys is to use an alloy reference with a similar composition to the analysis sample, and the next best one is to use a calibration curve measured using a series of alloy reference materials with different compositions spanning the unknown composition. Quantitative analyses of Au-Cu and Co-Ni alloy systems studied by VAMAS-SCA Japan working group showed that the alloy reference is critical for the analysis of alloy material with high mass difference. [5-7] The quantification of Fe-Ni alloy films was reported to be a good candidate as a subject for international round robin test for the quantification of alloy films because the matrix effect is not so severe. [8]

In this study, the results of the CCQM P-98 pilot study on the measurement of relative compositions of Fe-Ni alloy films are reported. RSFs derived from an alloy reference sample are much better than those derived from pure Fe and Ni films to ensure the measurement equivalency of NMIs for the composition analysis of Fe-Ni alloy films.

2. PREPARATION OF THE SAMPLES

Production of the Specimens

The Fe-Ni alloy films were grown by an ion beam sputtering deposition facility at Korea research institute of standards and science (KRISS). The chemical state and composition of the deposited films could be analyzed by *in-situ* XPS connected to the deposition chamber. [9] The target materials were sputtered by a 1 keV Ar⁺ ion beam produced by a Kaufmann-type DC ion

gun and deposited on substrates at room temperature. Films were grown on 150 mm diameter Si (100) wafers rotating with a speed of about 30 revolutions per minute to improve the uniformity. Thin films grown on silicon wafers were divided into 10 mm x 10 mm specimens. The specimens taken from near the center or the edge of the wafer were not used as test specimens. Three alloy films with nominal compositions of Fe₂₈-Ni₇₂, Fe₅₁-Ni₄₉, and Fe₇₈-Ni₂₂ have been produced. The film thicknesses of the Fe₂₈-Ni₇₂, Fe₅₁-Ni₄₉, and Fe₇₈-Ni₂₂ films determined from the C₆₀ SIMS depth profiles calibrated by the crater depth measured using a stylus profilometer were about 209.9, 207.4 and 199.9 nm, respectively. [8] The Fe-Ni alloy/Si interfaces in the SIMS depth profiles of the three alloy films were determined from the position where the intensity of Fe becomes half value between the intensity in the alloy film and the maximum intensity.

Certification of the Composition by ICP-MS

The composition of the Fe-Ni alloy films was certified by inductively coupled plasma-mass spectrometry (ICP-MS) with isotope dilution method.[8] Table 1 shows the certified compositions and their uncertainties of the three alloy films. The composition of the Fe-Ni alloy films was also analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES). The linear fitting of the results by ICP-MS and ICP-OES shows a slope of 0.999 and an offset of 0.110 % as shown in Figure 1. This quantitative correlation of the two results by the two primary methods supports that the certification result is reliable.

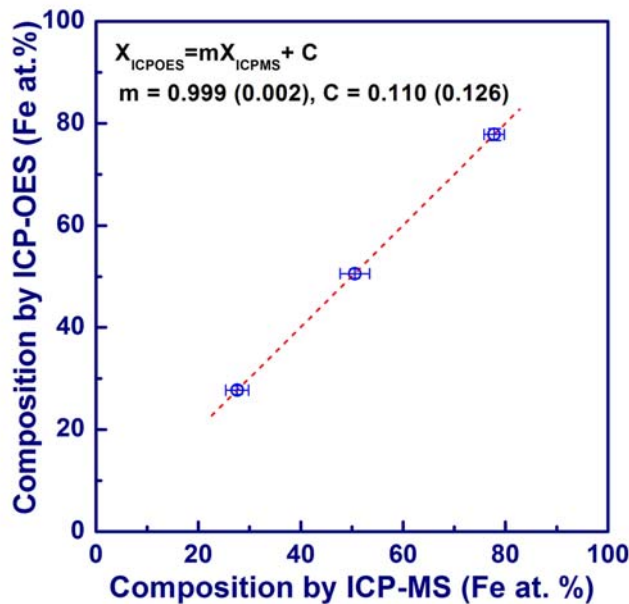


Figure 1. Linear fitting of the fractions of the Fe-Ni alloy films by ICP-MS and ICP-OES.

Table 1. The certified compositions and uncertainties of the three Fe-Ni alloy film CRMs.[8]

CRM	Fraction (Fe atomic %)	Uncertainty (Fe atomic %)
Fe28-Ni72	27.58	2.24
Fe51-Ni49	50.58	2.86
Fe78-Ni22	77.80	1.98

Homogeneity of Composition

The in-depth homogeneity of the composition of the Fe-Ni alloy films was investigated by SIMS depth profiling analysis. The SIMS depth profiling was performed with a Cameca IMS 4F where a commercial buckminsterfullerene C_{60}^+ ion source (IOG-C60-10; Ionoptica) is interfaced to the magnetic sector SIMS instrument. [10,11] Figure 2 is a depth profile of the Fe51-Ni49 alloy film. The relative fractions of Fe and Ni are uniform with depth except for a transient region near the surface and the interface. The relative sensitivity factors (RSFs) of Fe (R_{Fe}^{al}) and Ni (R_{Ni}^{al}) were measured from the average ion intensity of Fe (I_{Fe}^{al}) and Ni (I_{Ni}^{al}) divided by the certified fraction of Fe (C_{Fe}^{al}) and Ni (C_{Ni}^{al}) by the equations $R_{Fe}^{al} = I_{Fe}^{al} / C_{Fe}^{al}$, $R_{Ni}^{al} = I_{Ni}^{al} / C_{Ni}^{al}$, over the depth interval from 50 nm to 150 nm. The measured R value ($R = R_{Ni}^{al} / R_{Fe}^{al}$) is 3.229. The composition of an unknown alloy film can be calculated from the following equations.

$$X_{Fe}^{unk} = \frac{I_{Fe}^{unk}}{I_{Fe}^{unk} + I_{Ni}^{unk} / R} \quad \text{----- (1)}$$

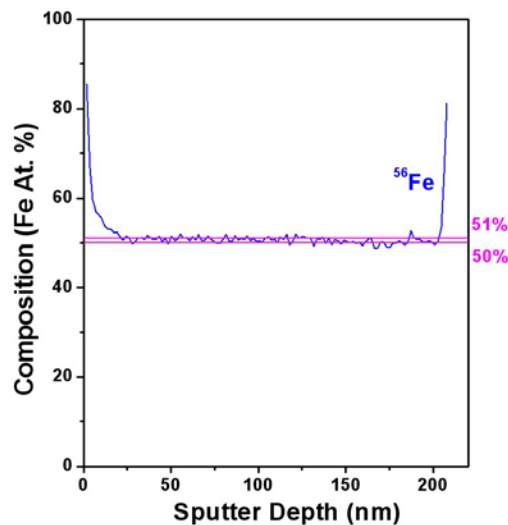


Figure 2. SIMS depth profile of the Fe51Ni49 film to confirm the in-depth uniformity.

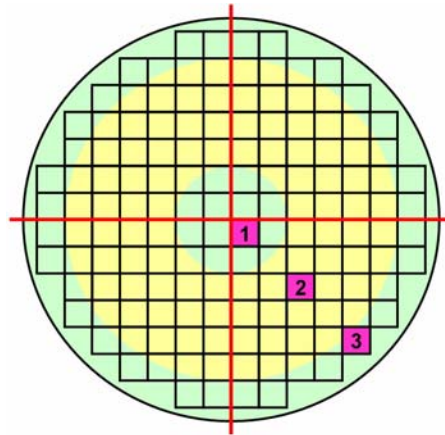


Figure 3. Dicing method of a Fe-Ni alloy film on Si(100) wafer. The number means the positions of specimens used to confirm the lateral homogeneity.

The original SIMS depth profiles of the three alloy films were converted to composition depth profiles using equation (1). The lateral homogeneity of the composition of Fe-Ni alloy films was also investigated by SIMS depth profiling using a C_{60}^+ ion source. The wafers were cut to small specimens of 10 mm x 10 mm size as shown in Figure 3.

The specimens in the yellow region were used as the test and reference specimens in this pilot study. The compositions of the specimens on the same radial position are expected to be homogeneous because the wafers were rotating during the deposition. Therefore, the lateral homogeneity due to the different radial distance from the center was taken into account.

Table 2. Intensities for Fe and Ni and relative fractions of Fe for three alloy specimens with different radial positions as designated in Figure 3.

Sample Position No.	I_{Fe}	I_{Ni}	Fe Fraction (atomic %)
1	1759	6141	50.57
	1897	6582	50.73
	1875	6529	50.64
	average		50.64
2	1803	6321	50.47
	1688	5875	50.65
	2310	8038	50.65
	average		50.59
3	1725	6012	50.61
	1675	5862	50.51
	1782	6183	50.73
	average		50.62

Table 2 shows the relative compositions of the three Fe51-Ni49 alloy specimens with different radial positions designated in Figure 3. The compositions of the specimens in the different radial positions are homogeneous within a relative standard deviation of 0.05 %.

3. OUTLINE OF THE PILOT STUDY

A. Objective, Timetable and Participation

The objective of the CCQM P-98 pilot study is to determine the compositions of Fe-Ni alloy films and to compare the equivalency of NMIs in the measurement of the composition of alloy films. There was no limitation in choosing an analytical technique for the quantification of alloy films. In April 2005, the quantification of Fe-Ni alloy films was suggested as a new subject for the pilot study in CCQM SAWG. After certification of the reference sample by ICP-MS and confirmation of the uniform in-depth distribution of the composition by SIMS depth profiling with a C₆₀ ion source, it has been approved as a project for pilot study in the CCQM meeting April 2006. The protocol and the test specimens have been delivered to the participants by the end of January 2007. The results of the pilot study were gathered by 15 March 2007 and reported at the CCQM meeting in April 2007. Additional data have been gathered by the end of June 2007. In the CCQM P-98 pilot study, 9 laboratories including 5 NMIs, three companies and one university participated as shown in Table 3.

Table 3. Participants in P98.

No.	Organisation	Country	Participants
1	NMIJ	Japan	T. Hayashi, T. Fujimoto
2	SAIT	Korea	S. Heo
3	Hynix	Korea	C. S. Jeong
4	NMISA	S. Africa	W. Jordaan, M. van Staden, S. Prins
5	Chungbuk Univ.	Korea	H. J. Kang
6	KRISS	Korea	D. W. Moon, K. J. Kim
7	LG-Elite	Korea	J. H. KIM
8	BAM	Germany	T. Gross, M. Procop, D. Schmidt, T. Wirth, W. E. S. Unger
9	NIM	China	H. Wang, X. P. Song

B. Cleaning of Contaminated Surface Layer

Dust and particles on the sample surface may be removed before introducing the samples into the analysis chamber. Surface contamination layer should be also removed by ion beam sputtering (e.g. with an Ar^+ ion beam). The surface oxide layer needs to be removed by ion beam sputtering so that the peak intensities, O 1s and C 1s, are minimized. Sputtering to reduce the relative ratio for $I(\text{C } 1s)/I(\text{Fe } 2p_{3/2})$ to less than 0.025 is recommended for quantitative surface analysis. [12] A similar reduction is required for the O 1s peak intensity. Quantitative analysis should be performed when the steady state is reached in course of sputtering. The steady state has been reached when all of the surface contaminants are eliminated and the surface composition does not change by further sputtering. Fortunately, in the quantitative analysis of Fe-Ni alloy films, the change of surface compositions, arising from preferential sputtering, was found to be negligible in the sputtering by 5 keV Ar^+ ions at 60° from the surface normal.[8]

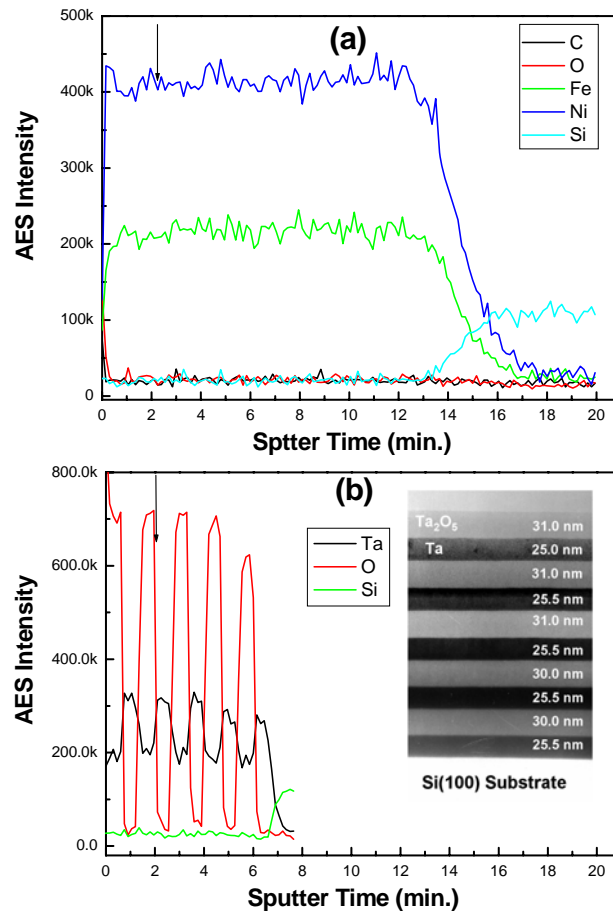


Figure 4. AES depth profiles of the Fe51-Ni49 film (a) and the Ta₂O₅/Ta multilayer (b) obtained at the same sputtering conditions (3 keV, 45 degree).

In P98 pilot study, a Ta₂O₅/Ta multilayer was used as a reference film to find the sputter conditions where the steady state is reached. The effective sputtering time necessary to reach the steady state can be determined from comparison of the depth profiles of the Ta₂O₅/Ta multilayer and the test specimens under the same sputtering conditions. Figure 4 shows AES depth profiles of the Fe51-Ni49 film and the Ta₂O₅/Ta multilayer obtained at the same sputtering conditions (3 keV, 45 degree).

The sputtering rate of the Ta₂O₅/Ta multilayer was 2.9 times faster than that of the Fe51-Ni49 film. The carbon and oxygen peaks were removed completely at the beginning of sputtering (0.5 min.) within the sputtering time to eliminate the first Ta₂O₅ layer (0.66 min.). Therefore, the sputtering time to the second Ta₂O₅ layer (arrows in Figure 4) was found to be enough for the elimination of surface contaminated layer and saturating sputtering for the quantification. The sputtering conditions for the Fe78-Ni22 and Fe28-Ni72 films may be similarly determined by the same method.

C. Quantification Methods

(1) Determination of RSFs from pure Fe and Ni films

Quantification by RSFs determined from pure elements is a general method to measure the composition of alloy films. In P98 pilot study, RSFs of Fe (R_{Fe}^{∞}) and Ni (R_{Ni}^{∞}) could be determined from the peak intensities of pure Fe (I_{Fe}^{∞}) and Ni (I_{Ni}^{∞}) films.

$$R_{Fe}^{\infty} = I_{Fe}^{\infty}, R_{Ni}^{\infty} = I_{Ni}^{\infty} \text{-----} (2)$$

The relative fraction of Fe in an alloy film (X_{Fe}^{al}) can be derived from the peak intensities of Fe (I_{Fe}^{al}) and Ni (I_{Ni}^{al}) by the following equations using R_{Fe}^{∞} and R_{Ni}^{∞} without correction of the matrix effect.

$$X_{Fe}^{al} = \frac{(I_{Fe}^{al}/R_{Fe}^{\infty})}{(I_{Fe}^{al}/R_{Fe}^{\infty}) + (I_{Ni}^{al}/R_{Ni}^{\infty})} \text{-----} (3)$$

(2) Determination of RSFs from an alloy film

The compositions of alloy films can be also analyzed by the relative sensitivity factors determined from an alloy film. The relative sensitivity factors of Fe (R_{Fe}^{al}) and Ni (R_{Ni}^{al}) were determined from the peak intensities of Fe (I_{Fe}^{al}) and Ni (I_{Ni}^{al}) divided by the certified fractions of Fe (C_{Fe}^{al}) and Ni (C_{Ni}^{al}) by the following equations.

$$R_{Fe}^{al} = (I_{Fe}^{al} / C_{Fe}^{al}), R_{Ni}^{al} = (I_{Ni}^{al} / C_{Ni}^{al}) \text{-----} (4)$$

The fractions of alloy films ($X_{Fe}^{\infty}, X_{Ni}^{\infty}$) measured by the RSFs determined from pure metal films can be converted to new values (X_{Fe}^{al}, X_{Ni}^{al}) by the conversion factors (F_{Fe}^{al}, F_{Ni}^{al}) derived from an alloy film by the following equations.

$$F_{Fe}^{al} = (X_{Fe}^{\infty} / C_{Fe}^{al}), F_{Ni}^{al} = (X_{Ni}^{\infty} / C_{Ni}^{al}) \text{-----} (5)$$

$$X_{Fe}^{al} = \frac{(X_{Fe}^{\infty} / F_{Fe}^{al})}{(X_{Fe}^{\infty} / F_{Fe}^{al}) + (X_{Ni}^{\infty} / F_{Ni}^{al})} \text{-----} (6)$$

In this study, the compositions of the Fe28-Ni72 and Fe78-Ni22 films were investigated using RSFs determined from the Fe51-Ni49 film.

D. Data Treatment

To determine the compositions of Fe-Ni alloy films and to compare the equivalency of NMIs in the measurement of the composition of alloy films, the measured compositions should be quantitatively correlated with the certified values. The compositions of the alloy films were measured by various analysis methods using two types of RSFs derived from the Fe51-Ni49 alloy film (R_{Fe}^{51} and R_{Ni}^{51}) or pure Fe and Ni films (R_{Fe}^{∞} and R_{Ni}^{∞}). The measured component fractions were linearly fitted as a function of the certified fractions by a linear least square fitting. The linear fitting results were expressed by the following equation.

$$X_{meas} = mX_{cert} + c \text{-----} (7)$$

Here, the offset c is the excess fraction when the certified fraction is extrapolated to zero and the slope m is a scaling constant. The ideal values of m and c are 1 and 0, respectively. The slope and offset values determined by participating laboratories were compared each other.

4. RESULTS AND DISCUSSIONS

A. X-ray Photoelectron Spectroscopy

7 laboratories involved in the quantification of Fe-Ni alloy films by XPS.

(1) KRISIS obtained the XPS spectra by a VSW 5000 using Mg K α X-ray source with the electron pass energy of 10 eV and the energy step of 0.1 eV. The surfaces of the films were cleaned by sputtering with 5 keV Ar⁺ ion beam of 60° incidence angle for 60 - 120 minutes on the raster size of 5 mm x 10 mm. Figure 5 shows Fe 2*p* and Ni 2*p* core level spectra of the Fe51-Ni49 alloy film. The binding energies of Fe 2*p*_{3/2} (E_b^{Fe}) and Ni 2*p*_{3/2} (E_b^{Ni}) are 706.7 eV and 852.6 eV, respectively. The relative intensities of the two elements were measured from peak areas by integration of the two peak intensities after peak smoothing and background subtraction by the Shirley method.[13] The integration ranges for the area measurement were from $E_b^{\text{Fe}} + 9$ eV to $E_b^{\text{Fe}} - 5$ eV and from $E_b^{\text{Ni}} + 11$ eV to $E_b^{\text{Ni}} - 5$ eV for the Fe 2*p* and Ni 2*p* peaks, respectively. The RSFs were derived from pure Fe and Ni films by equation (2) and the fractions of the constituent elements in the alloy films were calculated by equation (3).

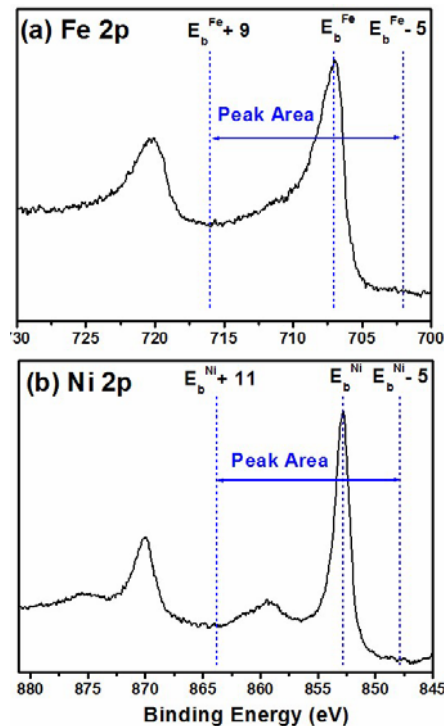


Figure 5. Fe 2*p* and Ni 2*p* core level spectra of the Fe₅₁-Ni₄₉ alloy film. The broken lines indicate the period of integration to determine the peak areas.

(2) NMISA used a Physical Electronics Quantum 2000 involving Al K α X-rays for the quantification of Fe-Ni alloy films. The energy scale of the XPS instrument was calibrated by analyzing a pure copper sample. After removing the samples from their respective holders, they were immediately loaded into the system. The system was allowed to pump down to 6.7×10^{-9} mbar or better. The distance between the analyser and each sample was optimized and five analysis points per sample, close to the centre of each sample, were chosen. The samples were sputtered for 1 min at 5 keV and 1 mm x 1 mm prior to analysis. The peak areas were selected on a consistent basis as with the reference materials using an Iterated Shirley background.

(3) NMIJ used XPS for the quantification. The XPS spectra were obtained with a VG Scientific ESCALAB 220i-XL using Mg K α x-ray source with the pass energy of 30 eV and energy step of 0.1 eV. The surfaces have been cleaned by sputtering with 3 keV Ar ion beam for 20 – 30 minutes.

(4) Hynix Semiconductor obtained XPS spectra by a VG Scientific ESCALAB 220i-XL using Mg K α X-ray source with pass energy of 30eV and energy step of 0.1eV. The surfaces were cleaned by sputtering using 3 keV Ar ion beam with the incidence angle of 60°.

(5) LG-Elite used a PHI5400 using Mg K α X-ray source. The surface has been cleaned by sputtering with 3 keV Ar⁺ ion beam for 60 minutes on the raster size of 4 mm x 4 mm.

(6) BAM obtained XPS data using an AXIS Ultra DLD XPS spectrometer manufactured by Kratos Analytical, UK. The binding energy scale of the instrument was calibrated following a Kratos analytical procedure which uses ISO 15472 binding energy data. XPS was done employing non-monochromatized Mg x-rays. Spectra were taken by setting the instrument to (i) the hybrid lens mode, and (ii) the slot mode providing approximately a 300 x 700 μm^2 analysis area. Seven measurements are made for each sample. The XPS measurements were performed after sputtering the surface with argon ions (4 keV) until the intensity ratio $I(\text{C } 1s) / I(\text{Fe } 2p_{3/2})$ is less than 0.025. The relative sensitivity factors were determined using the provided Fe and Ni films.

(7) NIM used XPS with a VG Scientific ESCALAB 220i-XL using Mg K α X-ray source with the pass energy of 20 eV. The fractions were determined from the peak areas of the Fe 2*p* and Ni 2*p* core level spectra. The RSFs of Fe and Ni were derived from the average intensities of six measurements for the pure Fe and Ni film. Before XPS analysis, a set of analysis samples as

received was sputtered for 10 minutes with 4 keV Ar⁺ ion beam of 50° incident angle to remove surface contaminants. Thus, the relative ratios for I(C 1s) / I(Fe 2p_{3/2}) were less than 0.025. A similar result was obtained for the O 1s peak intensity.

Table 4. CCQM P98 results of Fe atomic fraction [at. %] by XPS.

(a) using RSFs determined from pure Fe and Ni films.

No	Fe28-Ni72	Fe51-Ni49	Fe78-Ni22	Slope m	Offset c (at. %)
1	28.34	51.06	77.91	0.987	1.124
2	30.59	53.74	80.51	0.994	3.287
3	30.33	53.49	79.63	0.981	3.483
4	28.00	50.19	78.36	1.003	0.001
5	27.30	49.00	77.20	0.995	-0.555
6	27.70	51.50	76.90	0.978	1.176
7	25.80	53.00	78.10	1.038	-1.652
Average	28.29	51.71	78.37	0.997	0.981
Stdev	1.69	1.78	1.29	0.020	1.910

(b) using RSFs determined from Fe51-Ni49 alloy film.

No	Fe28-Ni72	Fe51-Ni49	Fe78-Ni22	Slope m	Offset c (at. %)
1	27.95	50.58	77.58	0.988	0.651
2	27.97	50.58	78.45	1.006	0.029
3	27.92	50.58	77.67	0.991	0.542
4	28.32	50.58	78.62	1.003	0.379
5	28.57	50.58	78.29	0.991	0.967
6	26.97	50.58	76.24	0.980	0.321
7	23.99	50.58	76.40	1.041	-3.781
Average	27.38	50.58	77.61	1.000	-0.127
Stdev	1.58	0.00	0.96	0.020	1.637

Slope m and offset value c determined by a linear least square fitting of the average compositions alloy films measured by XPS were investigated. CCQM P98 results by XPS are tabulated in Table 4. The average values of slope m and offset value are 0.997 and 0.981 %, respectively. The average values of slope m and offset values are greatly improved to m=1.000 and c=-0.127 % by conversion of the original compositions to modified compositions based on the RSFs derived from the Fe51-Ni49 alloy film by equation (5) and (6).

B. Auger Electron Spectroscopy

4 laboratories involved in the quantification of Fe-Ni alloy films by AES.

(1) Chungbuk national university used a Physical Electronics Model 700 Scanning Auger Nanoprobe system for the quantification of Fe-Ni alloy films by AES. 10 keV electrons with an electron beam current of 10 nA were used as a primary electron beam. The relative energy resolution of the CMA was 3%. Surface contaminants were removed by 3.0 keV Ar⁺ ion beam sputtering at an incidence angle of 45°. LMM Auger electron transitions of Fe (654 eV) and Ni (849 eV) were used for quantitative analysis. The RSFs of Fe and Ni ($RSF_{Fe^{\infty}}$ and $RSF_{Ni^{\infty}}$) were derived from the average values of three measurements for the pure Fe and Ni films. The RSFs and fraction of the constituent elements in the alloy sample were calculated by equations (2) and (3), respectively. Figure 6 shows Auger spectra of the Fe51-Ni49 alloy film. The intensity of Fe and Ni was determined from the peak-to-peak heights of the derivative spectra of the Fe LMM and Ni LMM transitions. In AES quantification, Shimizu and Ichimura's formula is used for the backscattering factor.[14] The inelastic mean free paths are derived from the TPP-2M equation.[15,16]

(2) SAIT used AES with a VG microlab 350 model. The experiments were performed at primary electron energy of 10 keV. The relative energy resolution of the CHA was 0.5%. The surfaces were cleaned by sputtering using 1 keV Ar ion beam for 30seconds with the raster size of 1mm × 1mm. LMM Auger electron transitions of Fe(654eV) and Ni(849 eV) were used for quantitative analysis.

(3) Hynix Semiconductor used PHI670 of Physical Electronics with 10 keV electron beam for the quantification by AES. The surfaces were cleaned by sputtering using 3 keV Ar ion beam with the incidence angle of 30°. The binary alloy compositions were calculated using the elemental RSFs of the constituent elements and normalization to 100 %. The RSFs of Fe and Ni were derived from the average intensities of five measurements for the pure Fe and Ni film.

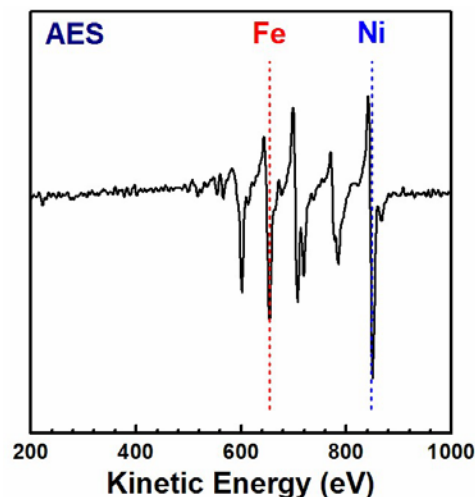


Figure 6. Auger spectra of the Fe51-Ni49 alloy film.

(4) BAM obtained AES data using Scanning Auger Microprobe model 595 from Physical Electronics (USA). 3 keV electron beam with 400 nA current was rastered on 50 μ m x 50 μ m. The angle between electron beam and surface normal was 30°. The surface was sputtered by 4 keV Ar⁺ ions after each spectrum acquisition for about 2sec. The angle between ion beam and surface normal was 34.1°. The sputter time was about 2.4 min, which was determined as proposed by using the delivered Ta₂O₅ sample.

Table 5 shows the CCQM P98 results by AES. In the case of quantification by RSFs determined from pure metal films, the average values of slope m and offset values are 1.006 and 1.041 %, respectively. Although the average slope m slightly increases from 1.006 to 1.009, the offset value is substantially reduced from 1.041 at. % (RSFs determined from the pure metal films) to 0.275 % by RSFs determined from the Fe51-Ni49 alloy film.

Table 5. CCQM P98 results of Fe atomic fraction [at. %] by AES.

(a) using RSFs determined from pure Fe and Ni films.

No	Fe28-Ni72	Fe51-Ni49	Fe78-Ni22	Slope m	Offset c (at. %)
1	29.00	49.60	77.90	0.974	1.51
2	30.26	53.32	80.92	1.009	2.383
3	29.03	50.95	80.49	1.027	0.124
4	28.18	51.44	79.16	1.015	0.148
Average	29.12	51.33	79.62	1.006	1.041
Stdev	0.86	1.54	1.37	0.023	1.104

(b) using RSFs determined from Fe51-Ni49 alloy film.

No	Fe28-Ni72	Fe51-Ni49	Fe78-Ni22	Slope m	Offset c (at. %)
1	29.83	50.58	78.51	0.971	2.491
2	27.99	50.58	79.17	1.02	-0.45

3	28.73	50.58	80.26	1.028	-0.247
4	27.49	50.58	78.59	1.018	-0.695
Average	28.51	50.58	79.13	1.009	0.275
Stdev	1.02	0.00	0.81	0.026	1.489

C. Electron Probe Microanalysis (EPMA)

In case of EPMA, the composition and film thickness (mass coverage) were determined. X-ray spectra were measured with an EDS (Thermo-Noran NSS) attached to a scanning electron microscope Zeiss Supra 40. For the determination of film compositions, a special commercially available program (STRATAGEM) was applied to evaluate the raw data. The principle of this kind of thin film analysis consists in measurement of electron excited X-ray spectra at different beam voltages for the specimen and the standards. The program fits the calculated intensity ratios versus high voltage to get composition and mass coverage. Spectra were measured for 12.5, 15, 20, 25 and 30 kV. No surface treatment was performed. The method described above does not need relative sensitivity factors. There is no normalisation to 100% of concentration. Instead any deviation from 100% means a check for the correctness of the result.

Table 6 show the CCQM P98 results by EPMA using RSFs from pure metals and those from an alloy film. The slope of the original fractions of FeNi alloy films measured by EPMA is slightly improved from 1.018 to 1.011 and the offset value was greatly improved -2.335 to 0.249 using the RSFs determined from Fe51-Ni49 alloy film.

Table 6. CCQM P98 results of Fe atomic fraction [at. %] by EPMA.

(a) using RSFs determined from pure Fe and Ni films.

Fe28-Ni72	Fe51-Ni49	Fe78-Ni22	Slope m	Offset c (at. %)
26.40	47.90	77.40	1.018	-2.335

(b) using RSFs determined from Fe51-Ni49 alloy film.

Fe28-Ni72	Fe51-Ni49	Fe78-Ni22	Slope m	Offset c (at. %)
26.40	47.90	77.40	1.011	0.249

D. Summary of the results

The measured slope and offset values of all data are plotted in Figure 7. The scattered data sets derived in the compositions by RSFs determined from pure metal films (a) are merged into the central area in those by RSFs determined from an alloy film (b). Especially the average offset value is substantially reduced from 0.725 to 0.038, which is very close to the ideal value of 0. This result means that the RSFs obtained from an alloy film are much more appropriate than those RSFs from pure metals for the quantification of alloy films and for the improvement of the equivalency in the measurement capabilities of participants, especially of NMIs.

The compositions of the Fe28-Ni72 and Fe78-Ni22 films determined by various analysis methods using two types of RSFs were compared in Table 7. The average fractions of Fe in the Fe28-Ni72 and Fe78-Ni22 films are improved from 28.41 at. % and 78.71 at. % to 27.86 at. % and 78.25 at. %, respectively, which are much closer to the certified values 27.58 at. % and 77.80 at. % as shown in Table 1. The compositions measured by XPS using RSFs determined from an alloy film show the minimum deviations from the nominal values as shown Table 4.

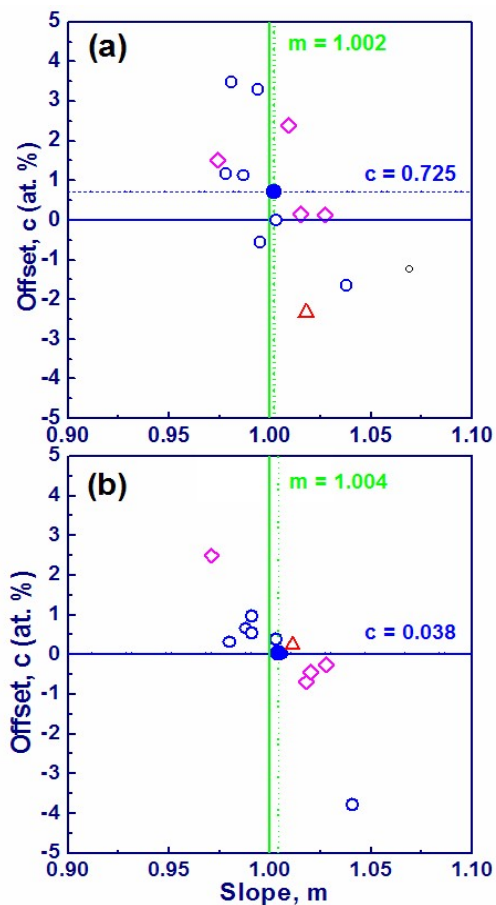


Figure 7. The measured slope m and offset c values derived from the compositions determined by using RSFs from pure metal films (a) and from an alloy film (b).

(\circ : XPS, \diamond : AES, \triangle : EPMA, \bullet : Average of all data)

Table 7. Compositions of the Fe28-Ni72 and Fe78-Ni22 films measured by various analytical methods using different RSFs.

RSF	Fe fraction (at. %)	
Nominal	27.58	77.80
$R_{Fe}^{\infty}, R_{Ni}^{\infty}$	28.41	78.71
R_{Fe}^{al}, R_{Ni}^{al}	27.86	78.25

5. CONCLUSION

CCQM P-98 pilot study to determine the compositions of Fe-Ni alloy films and to ensure the measurement equivalency of NMIs was performed by 9 laboratories including 5 NMIs, 3 companies and 1 university. RSFs derived from an alloy reference sample were found to be much more appropriate than those from pure Fe and Ni films. Linear fitting results showed an average slope of 1.002 with a standard deviation of about 0.020. Although the slope value slightly increased, the offset value was substantially decreased from 0.725 at. % to 0.038 at. % by RSFs using an alloy reference film. The results of the pilot study showed that Fe-Ni alloy system is a good candidate as a subject for a CCQM key comparison.

References

1. M. P. Seah, *J. Vac. Sci. Technol. A* **22**, 1564 (2004)
2. M. P. Seah, S. J. Spencer, F. Bensebaa, I. Vickridge, H. Danzebrink, M. Krumrey, T. Gross, W. Oesterle, E. Wendler, B. Rheinländer, Y. Azuma, I. Kojima, N. Suzuki, M. Suzuki, S. Tanuma, D. W. Moon, H. J. Lee, Hyun Mo Cho, H. Y. Chen, A. T. S. Wee, T. Osipowicz, J. S. Pan, W. A.

- Jordaan, R. Hauert, U. Klotz, C. van der Marel, M. Verheijen, Y. Tamminga, C. Jeynes, P. Bailey, S. Biswas, U. Falke, N. V. Nguyen, D. Chandler-Horowitz, J. R. Ehrstein, D. Muller, J. A. Dura, *Surf. Interface Anal.* **36**, 1269 (2004)
3. M. P. Seah, *Metrologia* **45**, *Tech. Suppl.* 08013 (2008)
 4. M. P. Seah, in "Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy", edited by D. Briggs and J. T. Grant, (IM Publications and Surface Spectra Ltd., 2003)
 5. D. Fujita, A. Tanaka, K. Koto, and T. Homma, *Surf. Interface Anal.* **16**, 183 (1990)
 6. A. Kurokawa, R. Shimizu, Y. Kubota, and H. J. Kang, *Surf. Interface Anal.* **14**, 388 (1989)
 7. M. Yoshitake, K. Yoshihara, Other members of the VAMAS-SCA working group in Japan, *Surf. Interface Anal.* **17**, 711 (1989)
 8. K. J. Kim, D. W. Moon, C. J. Park, D. Simons, G. Gillen, H. Jin and H. J. Kang, *Surf. Interface Anal.* **39**, 665 (2007)
 9. K. J. Kim, J. W. Kim, M. S. Yang and J. H. Jung, *Phys. Rev. B* **74**, 153305-1 (2006)
 10. G. Gillen, J. Batteas, C. Michaels, P. Chi, A. Fahey, J. Small, J. Verkouteren and K. J. Kim, *Appl. Surf. Sci.* **252**, 6521 (2006)
 11. K. J. Kim, D. Simons, and G. Gillen, *Appl. Surf. Sci.* **253**, 6000 (2007)
 12. Th. Gross, A. Lippitz, W. Unger and B. Gütler, *Surf. Interface Anal.* **29**, 891 (2000)
 13. D. A. Shirley, *Phys. Rev.* **B 5**, 4709 (1972)
 14. R. Shimizu, *Japan J. Appl. Phys.* **22**, 1631 (1983)
 15. S. Tanuma, C. J. Powell and D. R. Penn, *Surf. Interface Anal.* **21**, 165 (1994)
 16. M. P. Seah and I. S. Gilmore, *Surf. Interface Anal.* **31**, 835 (2001)