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Invited, Review

Uncertainty in Quantification of Binary Alloy Films and Thickness Measurement of nm Oxide Films

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Recent activities on the quantification of alloy films and the thickness measurement of ultra-thin oxide films are reviewed in this paper. The quantification and in-depth analysis are the main applications of surface analysis methods. However, surface analyses require certified reference materials because the determinations of the film thickness and the quantities of constituent elements by surface analysis methods are not absolute. International standardization on surface chemical analysis is focused on the establishment of traceability and the reduction of the measurement uncertainty. Pilot studies and key comparisons were performed for the measurements of the thickness of nm SiO_2 films and the chemical composition of binary alloy films by the surface analysis working group of the consultative committee for amount of substance.

1. INTRODUCTION

Uncertainty is a parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand. The reduction of uncertainty in surface analysis is the main purpose of the surface analysis working group (SAWG) of the consultative committee for amount of substance (CCQM). Key comparison is conducted to compare the equivalence of measurement capability of national metrology institutes (NMIs) and designated institutes (DIs). Generally, pilot study is performed first to confirm the feasibility of a key comparison.

Quantitative surface analysis is an important application of surface analysis techniques. Although XPS and AES are generally used for the quantitative surface compositional analysis of multi-component systems, it is typically difficult to obtain an accurate surface composition because of matrix effect.[1] Pilot study P-98 showed that the uncertainty in the quantification using the relative sensitivity factors of Fe and Ni derived from an alloy reference sample are much more appropriate than those from a pure Fe and a Ni film. The atomic fraction of a Fe-Ni alloy film and the uncertainty were compared in key comparison K-67 by four NMIs and a DI).[2-4]

Dielectric materials with equivalent thicknesses below 1 nm are required for the next- generation semiconductor device. However, metrology for the accurate thickness measurement of oxide films has not been fully established for the ultrathin oxides.[5] Pilot study P-38 and key comparison K-32 were conducted to compare the capabilities of NMIs for the thickness measurement of SiO_2 films with the nominal thicknesses in the range 1.5 nm to 8 nm. The measurand was the thickness of the silicon oxide layer on each of a total of 9 samples of nominal thicknesses in the range 1.5 to 8 nm on (100) and (111) Si substrates.[6,7]

In this paper, the various methods to improve the measurement uncertainty in surface analysis and the roles of certified reference materials (CRMs) are described. Moreover, some details of recent activities of CCQM SAWG on the quantification of alloy films and the thickness measurement of ultra-thin oxide films are reviewed.

2. FABRICATION OF SAMPLES

Thin film samples used in this study were fabricated by ion beam sputtering deposition system. Target materials were sputtered by 1 keV Ar^+ ion beam and deposited on substrate wafers. The ion beam sputter deposition chamber was connected to X-ray photoelectron spectroscopy (XPS) for the in-situ analysis of the surface composition and chemical state. The thin films grown on a transferable sample holder could be transferred to the analysis chamber without being exposed to air, and therefore the original chemical state, composition and impurities could be analyzed by *in-situ* XPS.

Various kinds of thin films could be grown by the combination of the target materials. Pure metal, oxide, multilayer and binary alloy thin films were developed. The thickness of the thin film layer was controlled by the growth time.

The growth rate was determined from the thickness of a preliminary thin film grown in a given time. The surface native oxide layer of substrate wafer was eliminated by rinsing in dilute HF solution. The thickness of the standard specimen for depth profiling was measured by HR-TEM, where the distance between the crystal planes can be a good internal standard for the measurement of the film thickness.

3. UNCERTAINTY IN QUANTIFICATION OF ALLOY FILMS

Fabrication and Certification of Fe-Ni Alloys

Fe-Ni alloy film CRMs were grown by sputtering deposition of two adjacent Fe and Ni targets. The relative compositions of Fe and Ni could be exactly controlled by the relative sputtering area of the two targets. After setting the right position of target holder by moving the targets, the alloy films were grown on 6 inch Si wafers.

Three alloy films with nominal target compositions of Fe28-Ni72, Fe51-Ni49, and Fe78-Ni22 were grown as a set of alloy films for the quantification study as shown in Figure 1. The photoelectron peaks of Fe and Ni were proportional to the compositions of the alloy films. No impurity peaks were detected.

The compositions of the alloy films were certified by inductively coupled plasma mass spectrometry (ICP-MS) as described in Table 1. The compositions were also measured by inductively coupled plasma optical emission spectroscopy (ICP-OES).

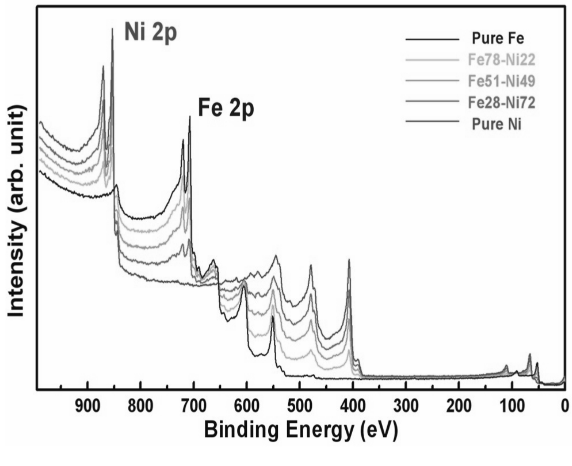

Figure 1. XPS survey spectra of the Fe-Ni alloy films. [2]

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

CRM	Fraction (Fe atomic %)	Uncertainty (Fe atomic %)
Fe28-Ni72	27.58	2.24
Fe51-Ni49	50.58	2.84
Fe78-Ni22	77.80	1.98

Figure 2 shows the relation between the compositions measured by the two absolute quantification methods. The results are well agreed within 0.1 %, which means that the certification results are reliable.

The in-depth and lateral homogeneity in the compositions of the Fe-Ni alloy films investigated by SIMS depth profiling was confirmed to be uniform. The compositions of the three Fe51-Ni49 alloy specimens at different radial positions were also homogeneous within the relative standard deviation of 0.05 %.

Quantification Methods

(1) Determination of sensitivity factors

Quantification by relative sensitivity factor (RSF) is a general method to measure the composition of alloy films. However, the uncertainty in the quantification by surface analysis is very high because the routine analysis is performed by the RSFs given by the vendors. Therefore, for the precise quantitative analysis, RSFs should be directly determined by using certified reference materials and the analysis should be performed under the same analysis conditions.

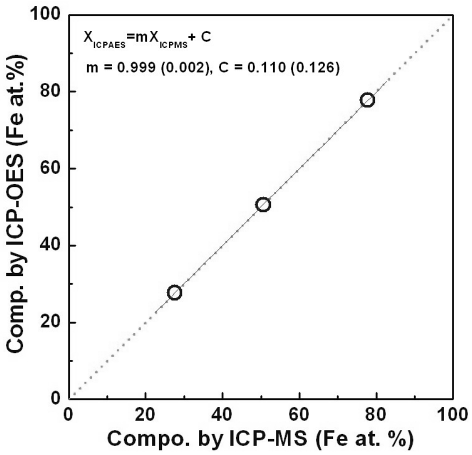

Figure 2. Certification of alloy composition by ICP-MS and ICP-OES. [2]

The RSFs can be determined by two methods. First one is pure element relative sensitivity factors (PERSFs). The PERSFs of Fe (S_{Fe}^{∞}) and and Ni (S_{Ni}^{∞}) are determined from the peak intensities of pure Fe (I_{Fe}^{∞}) and Ni (I_{Ni}^{∞}) films.

$$S_{Fe}^{\infty} = I_{Fe}^{\infty},\ S_{Ni}^{\infty} = I_{Ni}^{\infty} \text{ --------------------- } (1)$$

Second one is average matrix relative sensitivity factors (AMRSFs) with complete correction of matrix effect. The RSFs determined from an alloy reference can be supposed to AMRSFs. [8,9] The AMRSFs of Fe (S_{Fe}^{al}) and Ni (S_{Ni}^{al}) determined from the peak intensities of Fe (I_{Fe}^{al}) and Ni (I_{Ni}^{al}) divided by the certified atomic fractions of Fe (C_{Fe}^{al}) and Ni (C_{Ni}^{al}) of an Fe-Ni alloy reference film.

$$S_{Fe}^{al} = (I_{Fe}^{al}/C_{Fe}^{al}),\ S_{Ni}^{al} = (I_{Ni}^{al}/C_{Ni}^{al}) \text{------ (2)}$$

In the quantitative analysis of an alloy film, the relative ratios of AMRSFs determined by dividing the AMRSFs by a representative AMRSF are much more useful. In the case of Fe-Ni alloy, the relative ratios of AMRSFs of Fe (R_{Fe}^{al}) and Ni (R_{Ni}^{al}) are determined by the following equations.

$$R_{Fe}^{al} = S_{Fe}^{al}/S_{Fe}^{al} = 1,\ R_{Ni}^{al} = S_{Ni}^{al}/S_{Fe}^{al} \text{ ----- (3)}$$

(2) Quantification of the alloy films

The compositions (X_{Fe}^{∞}) of alloy films were determined by the PERSFs determined from pure Fe and Ni films by the following equation.

$$X_{Fe}^{\infty} = \frac{(I_{Fe}^{al}/S_{Fe}^{\infty})}{(I_{Fe}^{al}/S_{Fe}^{\infty}) + (I_{Ni}^{al}/S_{Ni}^{\infty})} \text{ -------------- (4)}$$

The compositions (X_{Fe}^{al}) of alloy films were also measured by the relative ratios of AMRSFs (R_{Fe}^{al}, R_{Ni}^{al}) by the following equation.

$$X_{Fe}^{al} = \frac{(I_{Fe}^{al}/R_{Fe}^{al})}{(I_{Fe}^{al}/R_{Fe}^{al}) + (I_{Ni}^{al}/R_{Ni}^{al})} \text{ -------------- (5)}$$

(3) CCQM Pilot Study P-98

The objective of the CCQM pilot study P-98 was to confirm the feasibility of measurement equivalency for the composition of alloy films by NMIs. P-98 was approved as a pilot study project in CCQM meeting April 2006. The protocol and the test specimens have been delivered to the participants by the end of January 2007. The results gathered by the end of June 2007. Participants were free to clean the samples with inert gas ion sputtering under their own chosen conditions. The Fe-Ni system was chosen for analysis since the close nature of its constituents should lead to the low level of preferential sputtering.[10]

9 laboratories participated in P-98 using XPS, AES and EPMA. The compositions of the alloy films were measured by various analysis methods using two types of sensitivity factors derived from the Fe51-Ni49 alloy film (R_{Fe}^{51} and R_{Ni}^{51}) or pure Fe and Ni films (S_{Fe}^{∞} and S_{Ni}^{∞}). The measured fractions were linearly fitted as a function of the certified fractions by a linear least square fitting by the following equation.

$$X_{meas} = mX_{cert} + c \text{ ----------------- (6)}$$

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.

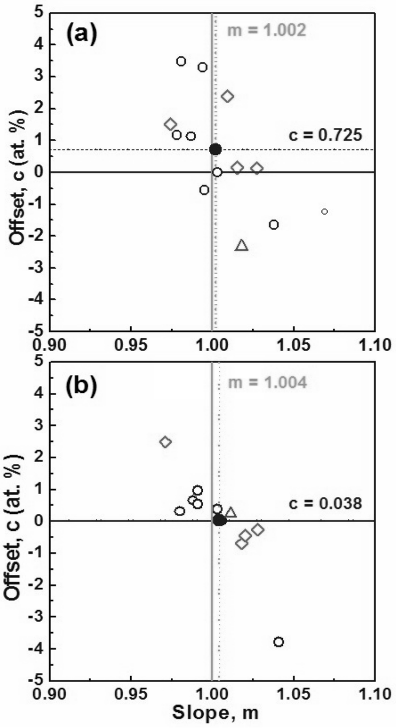

Figure 3. The slope and offset values derived from the compositions (a) by PERSFs from pure metal films, (b) by AMRSFs from an alloy film. [3]
(○: XPS, ◇:AES, △: EPMA, ●: Average)

The measured slope and offsets of all data are plotted in Figure 3. The scattered data derived in the compositions by PERSFs determined from pure metal films are merged into the central area in those by the relative ratios of AMRSFs determined from an alloy film. Especially the average offset value is greatly improved from 0.725 to 0.038. This result means that the AMRSFs obtained from an alloy film are much more appropriate than PERSFs from pure metals for the quantification of alloy films and for the improvement of the equivalency.

Table 2. An example of the uncertainty in the determination of RSFs.

No	I_{Fe}^{al}	I_{Ni}^{al}	S_{Fe}^{al}	S_{Ni}^{al}	S_{Ni}^{al}/S_{Fe}^{al}
1	51605	83179	102026	168310	1.650
2	48222	76822	95338	155447	1.631
3	44595	71978	88167	145645	1.652
4	45909	72041	90765	145773	1.606
5	45492	72975	89941	147663	1.642
6	45834	73221	90617	148161	1.635
Ave.	46943	75036	92809	151833	1.636
u (%)	2.24	2.38	2.24	2.38	0.42
u_{RSF} (%)	3.17		3.17		0.42

(4) Reduction of Measurement Uncertainty

In the quantitative analysis of alloy films by surface analysis methods, the combined standard uncertainty u_c is calculated from the equation

$$u_c^2 = u_{meas}^2 + u_{CRM}^2 \quad \text{----------------} \quad (7)$$

The first term ($u_{\rm meas}$) is the standard uncertainty in the measurement of the alloy composition by surface analysis. It is derived from the combination of the standard uncertainties in the determinations of RSFs ($u_{\rm RSF}$) and alloy composition ($u_{\rm All}$).

Table 2 shows an example of the standard uncertainty in the determination of RSFs from an alloy reference. The standard uncertainty in the determination of RSFs from the individual AMRSFs ($u_{\rm RSF}$=3.17 %) is greatly reduced in that from the relative ratios of AMRSFs ($u_{\rm RSF}$=0.42 %), which is due to the fact that the relative ratios of the intensities of Fe and Ni do not depend on the experimental conditions. The second term ($u_{\rm CRM}$) is the combined standard uncertainties of the certified compositions given in Table 1. The combined standard uncertainty u_c and the expanded uncertainty $U = ku_c$, with 95 % confidence level are tabulated in Table 2.

Table 3. Uncertainty table determined by RSFs using an ally reference.

Factor	Uncertainty (at. %)
$u_{\rm RSF}$ (%)	0.42
$u_{\rm All}$ (at. %)	0.26
$u_{\rm meas}$ (at. %)	0.34
$v_{\rm meas}$	5
$u_{\rm CRM}$ (at. %)	1.42
$v_{\rm CRM}$	∞
u_c (at. %)	1.46
$v_{\rm eff}$	449
k	1.97
U (at. %)	2.88

Table 4. Submitted values of CCQM-K67 with uncertainty at 95% confidence level. [4]

Participant	Method	x_i (at. %)	U_i (at. %)
BAM	AES	50.28	3.22
NIM	XPS	51.48	2.88
NMIJ	XPS	47.74	2.95
NMISA	XPS	50.25	3.40
KRISS	XPS	50.34	2.88
Average-		50.02	3.07

The effective degrees of freedom ($v_{\rm eff}$) were estimated from the Welch-Satterthwaite formula.[11] Table 3 shows that the uncertainty of CRM is the main factor in determination of the compositions of alloy films.

(5) CCQM Key Comparison K-67

CCQM SAWG K-67 key comparison was conducted on the quantitative analysis of a Fe-Ni alloy film. As a result of P-98, an alloy film was recommended to be used as a reference specimen. Four NMIs and one DI participated in K-67 and one DI participated in P-108, respectively.

The objective of K-67 and P-108 is to determine the atomic fractions of a Fe-Ni alloy film and to compare the international equivalence in the measurement. The required measurand was the atomic fraction of the alloy film expressed in atomic percent. As usual in CC comparisons, there was no limitation in choosing analytical techniques for quantitative analysis.

The submitted values (x_i) of the CCQM-K67 were measured as the atomic fraction of Fe as shown in Table 4. The expanded uncertainties in K-67 were ranged from 2.88 to 3.40 atomic %. The arithmetic mean value (50.02 at. %) was approved as the key comparison reference value (KCRV) and the uncertainty of KCRV calculated from the standard deviation of the individual values and a coverage factor (k) of 2 was 1.23 atomic %.

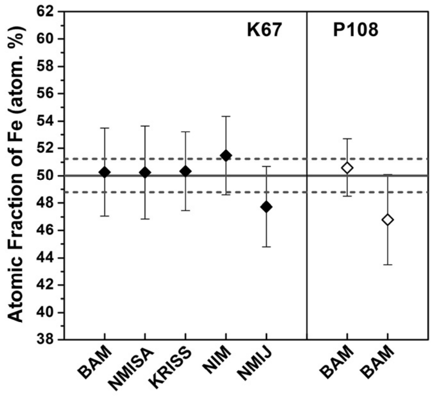

Figure 4. Key comparison reference value and uncertainties in CCQM K67/P108. [4]

Summary of Quantification of Alloy Films

A CCQM pilot study (P-98) and a key comparison (K-67) were conducted to determine the compositions of Fe-Ni alloy films and to ensure the measurement equivalency of NMIs. The purpose of the pilot study and the key comparison is to establish the traceability and uncertainty in the determination of the compositions of alloy films.

P-98 showed that the AMRSFs derived from an alloy reference film are much better than the PERSFs determined from a pure Fe and Ni films to improve the measurement equivalency of national metrology institutes.

The average uncertainty in the key comparison K-67 was 3.1 atomic %, which is the best value in the quantitative analysis of binary alloy films. The most important parameter to reduce the measurement uncertainty in the measurement of alloy composition was found to be the reduction of the uncertainty of CRM.

4. UNCERTAINTY IN MEASUREMENT OF THICKNESS OF NM OXIDE FILM

Thickness measurement of nm SiO_2 by XPS

The thickness of a SiO_2 overlayer (T_{ox}) on a Si substrate is determined from the Si 2p core level spectrum by the following equation.

$$T_{ox} = L\cos\theta\ln(R_{\exp}/R_0 + 1) \text{ ----------- } (8)$$

Here, L is the attenuation length of Si 2p in the SiO_2 matrix and θ is the angle between the surface normal and analyser. R_0 (= $I_{SiO2}^{\infty}/I_{Si}^{\infty}$) indicates the relative peak intensities of Si 2p measured from pure SiO_2 and pure Si. R_{exp} (= $I_{SiO2}^{exp}/I_{Si}^{exp}$) is the relative peak intensities of Si 2p measured from a SiO_2 overlayer on Si. If L, θ and R_0 are determined correctly by experiments or theoretical calculations, the thickness can be derived from the measurement of the R_{exp} value.

Pilot Study for Thickness Measurement (P-38)

Thickness of nm SiO_2 films were measured by various thickness measurement methods and compared in CCQM pilot study P-38. The measured thicknesses were linearly plotted and the slopes (m) and offset values (c) were compared. Figure 5 shows the offsets and standard deviations determined by various methods. Most of the methods show large offsets in the range of 0.5 nm ~ 1.0 nm. In the cases of ellipsometry and x-ray reflectometry (XRR), the surface contamination is a main source of the large offset.

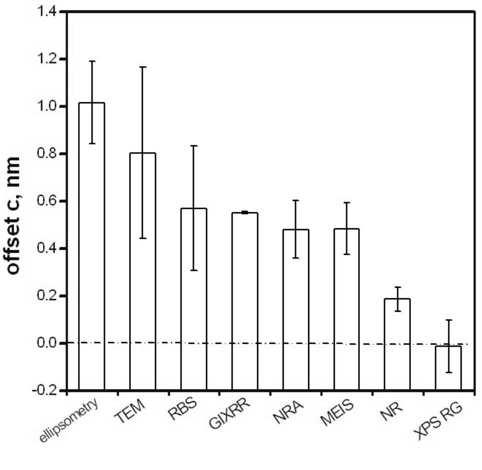

Figure 5. The offsets and standard deviations in the thicknesses measured by various methods. [6]

Water, carbon compound and adsorbed oxygen layer are another main contamination sources. In the case of TEM, the difficulties in the determination of the surface and interface locations are the sources of the large offset value. The choice of the appropriate capping layer and using of the right definition of interface are required.

The important point is that the offset value of XPS is close to 0. It is theoretically right because the amount of oxygen combined with silicon is converted to thickness of SiO_2 layer in XPS. If there is no silicon oxide, the thickness should be 0 from the thickness equation (8)

This was experimentally proved by in-situ XPS analysis of a series of SiO_2 films as shown in Figure 6. The measured thickness of SiO_2 films is linear to the nominal thickness controlled by growth time.[12]

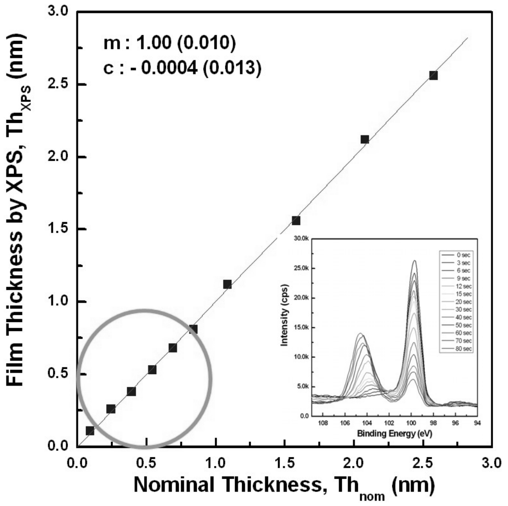

Figure 6. Linearity of the measured thickness and the nominal thickness of SiO_2 films. [12]

Key Comparison for Thickness Measurement of SiO_2 films on Si (K-32)

CCQM key comparison K-32 was performed to compare the equivalency on the measurement capability of NMIs for the measurement of silicon oxide on silicon wafer. 9 samples of nominal thicknesses in the range 1.5 to 8 nm on (100) and (111) Si substrates were used. 8 NMIs participated with XPS, neutron reflectometry (NR), XRR and ellipsometry. Figure 7 shows the K-32 results for SiO_2 films on Si (100) with the thicknesses of 1.5. 2. 4, 8 nm. The results by XPS (NPL, KRISS, BAM) shows a great equivalence with low level of uncertainty. Key comparison reference value and their associated uncertainties were determined from the weighted means and the expanded weighted standard deviations of the means.

Uncertainty in the Thickness Measurement by XPS [7]

The standard uncertainty in the measurement of thickness of nm silicon oxide films can be described by the following equation.

$$u_{meas}^2 = u_E^2 + u_n^2 + u_\theta^2 + u_A^2 + u_p^2 + u_F^2 + u_L^2 \text{--- } (9)$$

u_E: validity of the model
u_n: spectrometer signal
u_θ: angle setting
u_A: analyser electron optics
u_P: different numbers of peaks in the fitting

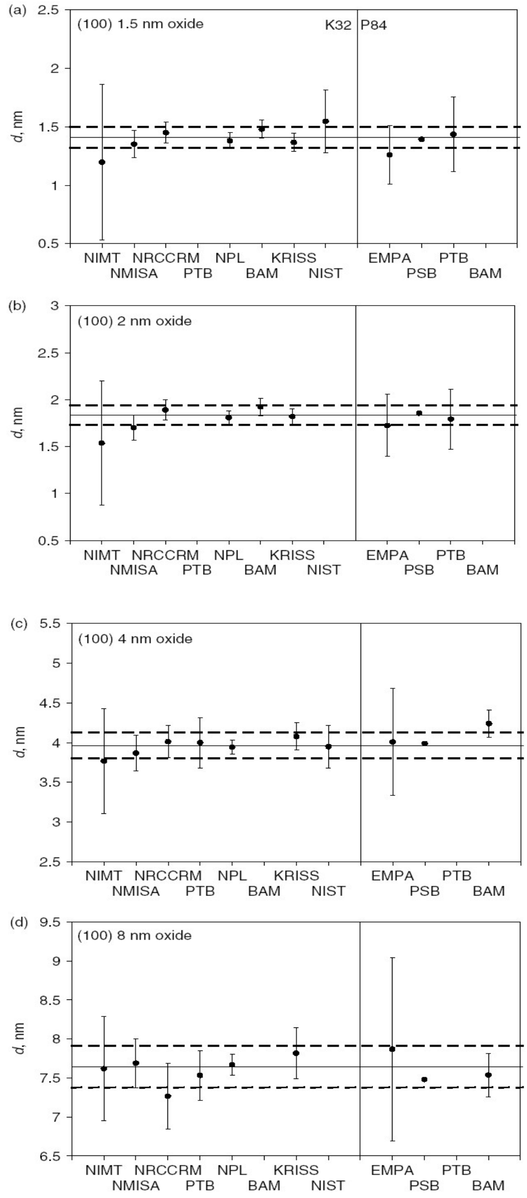

Figure 7. K-32 results for SiO_2 films on Si (100) with the thicknesses of 1.5. 2. 4, 8 nm. [7]

u_F: different peak shape algorithms
u_L: electron attenuation length

u_n and u_θ have random contributions (type A) and the other terms largely involve systematic contributions (type B). u_E is less than 0.025 nm and u_A is negligible for an analyser with small cone entrance angle. u_P and u_F are negligible for fitting five peaks using valid software.

However, if a certified reference film is used, the measurement process is simplified. The electron attenuation length is determined by equation (8) from the certified thickness and R_0. The thickness of the analysis sample is measured from the electron attenuation length using the same analysis conditions. In this case, most of the uncertainty parameters in equation (9) can be compensated and included in the uncertainty in the determination of the electron attenuation length. Due to the explanations below equation (9), equation (9) can be simplified as below,

$$u_{meas}^2 = u_L^2 + u_\theta^2 \text{ -------------------------- } (10)$$

This combined with equation (7) to be the next,

$$u_c^2 = u_{CRM}^2 + u_L^2 + u_\theta^2 \text{ -------------------- } (11)$$

(1) Determination of attenuation length

Determination of the attenuation length is critical for the thickness measurement of overlayers by XPS as shown in equation (8). The effective attenuation length of Si 2p electron in SiO_2 matrix has been reported in a wide range from 2 to 4 nm and predicted from the theoretical inelastic mean free path.[13-15] In P-38 and K-32, when R_o was taken as 0.9329, L values were 2.996 or 3.485 nm for Mg or Al Kα X-rays, respectively. The best way to determine the attenuation length is the direct measurement by equation (8) using a reference material.

Mutual calibration method was suggested as a method to determine the electron attenuation length and the thickness of oxide films. [16,17] It is based on the traceability in the length unit of TEM and the traceability in the offset value of XPS. In TEM, the thickness of oxide layer is determined by the lattice constant of Si (100) substrate. The lattice constant is traceable to length unit because it is determined by diffraction of x-ray light.

Figure 8 shows a schematic diagram of the mutual calibration method. The thickness of a series of SiO_2 films on Si (100) can be determined by linear fitting of the thicknesses determined by XPS and TEM from the following equation.

$$T_{TEM} = mT_{XPS} + c \text{ ------------------------- } (11)$$

Without calibration, slope (m) and offset (c) are far from the ideal values (m≠1 and c≠0) as shown in Figure 8. The offset of TEM should be subtracted because it is originated from the positions of the interface and the surface. And the slope of XPS should be calibrated because it is originated the wrong electron attenuation length. From the slope and offset, the thicknesses of TEM and XPS can be mutually calibrated to the certified thicknesses (T^c_{TEM}, T^c_{XPS}) by the following relations.

$$T_{TEM}^c = T_{TEM} - c \text{ ------------------------- } (12)$$

$$T_{XPS}^c = mT_{XPS} \text{ ---------------------------- } (13)$$

Figure 9 shows an example of the mutual calibration method to evaluate the electron attenuation length of Si 2p. By 1253.6 eV x-ray energy, the electron attenuation length is 2.994 ± 0.114 nm, and is found to be fully consistent with the previous value of 2.996 ± 0.016 nm [16] when the R_0 value of 0.9329 is applied in Equation (8)".

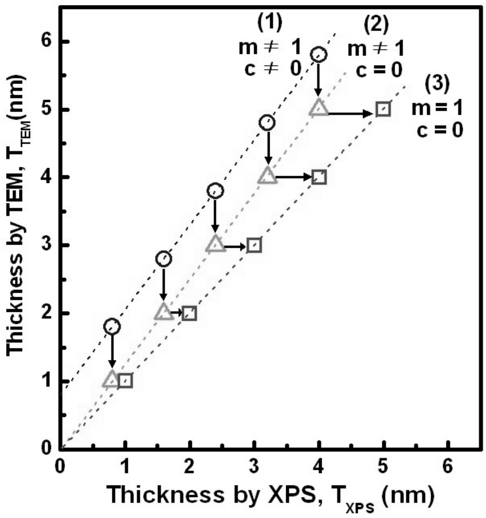

Figure 8. Certification of thickness by mutual calibration method. [16]

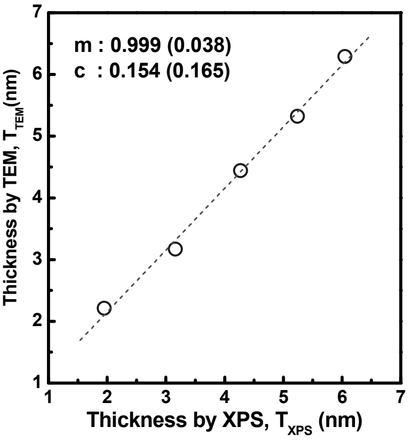

Figure 9. Example of mutual calibration method to determine the thickness of SiO_2 films. [16]

The thicknesses of Al_2O_3 films with an interfacial SiO_2 layers were also determined by the mutual calibration method.[17] XPS has been confirmed to be suitable as an offset-traceable method by showing that the offset value of XPS analysis for Al_2O_3 is small.

By 1253.6 eV x-ray source, the electron attenuation length of Al 2p was determined to be 2.4334 nm in Al_2O_3 when R_0 of 0.539 is applied. The measured electron attenuation length was close to the simulation result by TPP-2M equation.[17] The thickness of Al_2O_3 films with sub-nm thickness could be determined by mutual calibration method.

(2) Determination of Electron Emission Angle

In the determination of the thickness of SiO_2 overlayer on Si by XPS, the electron emission angle is one of the largest sources of the uncertainty. In the thickness measurement of nm SiO_2 film on Si (100), reference geometry (RG) is recommended to minimize the diffraction effect of the substrate. As shown in Figure 10, azimuthal angle of 22.5° and electron emission angle of 34° are the RG of Si (100) substrate. In this large polar angle, the shift of 1° emission angle results in the thickness variation of about 1.16 %.

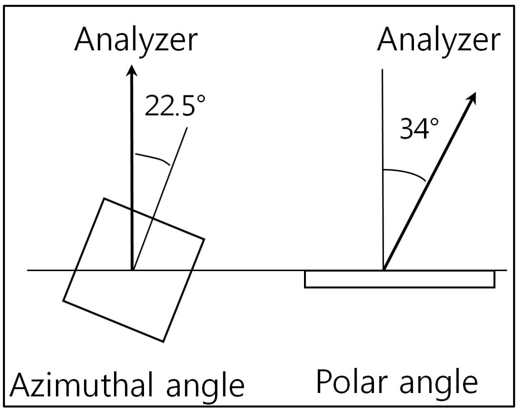

Figure 10. Reference geometry for the thickness measurement of oxide films on Si(100) substrate.

Although the electron emission angle could be controlled within 0.1 % accuracy by using a laser beam,[18] it is not easily applicable unless suitable windows are available in the instrument. The emission angle scale in most instruments is of undefined accuracy and may exhibit errors as high as 5% without calibration. The original axis of analyser may be somewhat different from the real one and the mechanical control of polar angle can be biased. Therefore the surface normal of the analysis system should be correctly determined for the precise control of electron emission angle.

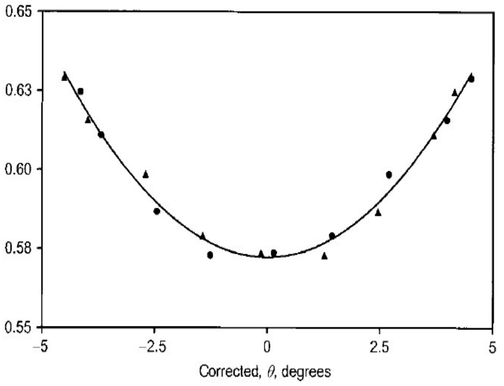

Figure 11. Concept of crystal axis method [18]

Two methods to determine surface normal were suggested. The crystal axis method (CAM); utilizes an electron diffraction effect of a Si (100) wafer as shown in Figure 11. The thickness of SiO_2 film is minimized along the [100] direction by Eq. (8) because the intensity of Si 2p from the Si (100) substrate is maximized. The angular offset (θ^0) from the surface normal is determined from the angle at which T_{ox} is minimized by the following equation.

$$T_{\mathrm{ox}} = b + a(\theta - \theta_0)^2 \text{ ------------------- } (14)$$

The overlayer thickness consistency method (OTCM) utilises the consistency obtained in the thickness of an amorphous SiO_2 overlayer on an amorphous Si substrate as shown in Figure 12.[19] The thicknesses of SiO_2 films on an amorphous Si substrate are measured at the emission angles of 10^{o}, 20^{o}, 30^{o} and 40^{o}.

When the surface normal is correctly set, the thicknesses measured at four different emission angles should be approximately the same. The angular offset is determined from the applied angle shift at which the relative standard deviation of the four thicknesses is minimized. Recently, however, a significant bias was reported in OTCM when the thicknesses are set exactly the same using equation (8) and it is recommended that the CAM be used.[20] Although the increase in the effective value of electron attenuation length due to the elastic scattering deflections was suggested as an origin of the bias, the reason of the significant bias is not still clear. The difference in the surface normal by CAM and OTCM should be clearly understood for the correct calibration of the surface normal.

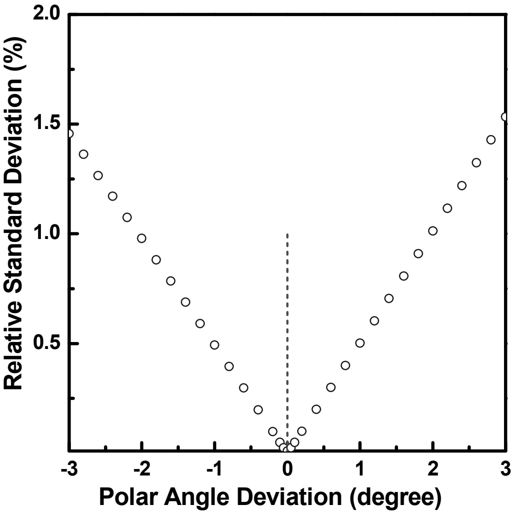

Figure 12. Concept of the overlayer thickness consistency method.[19]

5. CONCLUSION

The establishment of traceability and the reduction of the uncertainty on the surface chemical analysis are the main purposes of international standardization studies by CCQM SAWG.

A pilot study P-98 for the measurements of the chemical composition of Fe-Ni alloy films showed that the AMRSFs determined from an alloy reference film are much better than the PERSFs determined from a pure Fe and Ni films for the improvement of the measurement equivalency of NMIs and reduction of the measurement uncertainty. The average uncertainty in the key comparison K-67 was 3.1 atomic %. The standard uncertainty of the CRM is the most important parameter for the determination of the expanded uncertainty.

A pilot study P-38 and a key comparison K-32 were conducted for the thickness measurement of nm SiO_2 films. Although the offset values of thickness by most of the thickness measurement methods were large in the range of 0.5 nm ~ 1.0 nm, the offset value by XPS was close to zero. The zero offset value of XPS was experimentally elucidated by the film growth and in-situ XPS analysis. A mutual calibration method using XPS and TEM was suggested as a new method to certify the thickness of oxide films. The uncertainty in the thickness measurement can be simply and correctly determined using a CRM with a reliable certified thickness and an uncertainty.

Conclusively, certified reference materials are required for the determination of uncertainty in surface analysis because the measurements of the quantity and film thickness by surface analysis methods are not absolutely traceable.

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