CCQM-K157

Measurement of the amount of substance of HfO_2 expressed as the thickness of nm films

Final Report

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Abstract

CCQM key comparison K157 for the thickness measurement of HfO_2 films was performed by Surface Analysis Working Group (SAWG) of Consultative Committee for Amount of Substance (CCQM). The aim of K157 is to establish the measurement traceability and to ensure the equivalency in the measurement capability of national metrology institutes for the thickness measurement of HfO_2 films.

In this key comparison, the thicknesses of six HfO_2 films with the nominal thickness range from 0.7 nm to 6 nm were compared by x-ray photoelectron spectroscopy (XPS), x-ray reflectometry (XRR), transmission electron microscopy (TEM), spectroscopic ellipsometry (SE) and medium energy ion scattering spectrometry (MEIS).

1. Introduction

The thickness measurement of nanoscale SiO_2 films on Si substrates was the subject of the first key comparison K32 by the Surface Analysis Working Group (SAWG) of the Consultative Committee for Amount of Substance (CCQM) in 2004. As a result, the traceability for the thickness measurements of ultra-thin SiO_2 thin films on Si(100) and Si(111) substrates was established.

Before the key comparison K32, the thickness measurement results of nm SiO_2 films were compared in the pilot study P38 by various measurement methods such as SE, XRR, TEM, MEIS and XPS. In the linear fitting of the results to the nominal thicknesses, large offset values were found in the thickness values measured by means of physical methods such as SE, XRR, TEM and MEIS. The offset values were found to be attributed to surface contamination and the difficulty in the determination of the locations of the interfaces and surfaces. However, the offset value of XPS measured from the reference geometry was close to zero because the thickness of the SiO_2 layer depends on the chemical amount of oxide intensity derived from the SiO_2 layer.

A mutual calibration method was developed to determine the traceable thickness of the SiO_2 films on Si (100) substrate. In this method, XPS with zero offset value acts as a zero offset method and TEM or XRR act as length unit traceable methods where the thickness in length units is directly obtained. From the results, the mutual calibration method can be a traceable method that determines the thickness of nanoscale oxide films. The mutual calibration method was successively applied for the thickness measurement of various oxide films. Recently, thickness measurement by MEIS with the intensity of scattered ions has been probed as a useful zero offset method for the thickness measurement of hetero-oxide films.

Today, the thickness measurement of gate dielectric materials with a thickness of less than 1 nm is still one of the most important measurement issues for the continual scaling down of semiconductor devices. HfO_2 is a dielectric material that can be used as an alternative to SiO_2. Therefore, a traceable thickness measurement of ultrathin HfO_2 films by physical or chemical methods is required for advanced semiconductor industries.

In the CCQM SAWG meeting in April 2017, the thickness measurement of HfO_2 films was suggested as a new subject for CCQM pilot study P190. The protocol and the test specimens for P190 were delivered by June 2017 and the results were collected by November 2017. The report of P190 was published in Metrologia in June 2021. As a result of P190, K157 was launched as a key comparison for the thickness measurement of HfO_2 films.

2. Outline of CCQM-K157

2.1. Objective

The objective of this key comparison is to measure the thicknesses of the HfO_2 films with the nominal thicknesses from 0.7 to 6.0 nm on Si (100) substrates. The measurand of this key comparison is the amount of substance of HfO_2 expressed as the thickness of the HfO_2 films.

2.2. Participation

8 NMIs and 1 DI participated in CCQM key comparison K157 as shown in Table 1. XRR, XPS, TEM, MEIS, XRF and SE were used for the thickness measurement.

Table 1. Participants in CCQM K157.

No.	Organisation	Country	Method	Contact Person
1	BAM	Germany	XPS	J. Radnik
2	INMETRO	Brazil	TEM	B. S. Archanjo
3	KRISS	Korea	MEIS	K. J. Kim
4	NIM	China	XRR, XPS, TEM	Y. Yao
5	NIST	USA	XRR	D. Windover
6	NMIJ	Japan	XPS, XRR	H. Matsuzaki
7	NMISA	South Africa	XPS	W. A. Jordaan
8	NPL	UK	XPS, SE	A. G. Shard
9	PTB	Germany	XRR	M. Krumrey

3. The Specimens

A series of $HfO_2/SiO_2/Si(100)$ films with the nominal thicknesses of 0.7 nm, 1.0 nm, 2.0 nm, 3.0 nm, 4.0 nm and 6.0 nm were grown on the polished side of Si (100) substrates by atomic layer deposition. Before the growth of the HfO_2 films, 2 nm SiO_2 layer was grown on the Si (100) substrates by thermal oxidation to prevent the diffusion of oxygen atoms from the HfO_2 films to Si (100) substrate. The wafers were cut into small specimens with the size of 10 mm x 10 mm. The relative standard deviation of the film thickness determined by XPS analysis was lower than 1.2%. The deadline of K-157 was set at the end of June 2021. However, it was delayed to the end of September 2021 due to the delay of the delivery of the specimens by the pandemic in some countries.

4. Measurement Methods

The measured thicknesses have been submitted with uncertainties. The various contributions of the uncertainty budget were all stated in the reports. The measurement methods, instrument and procedures were also reported.

1) BAM/PTB

The thicknesses of the two thinnest films were measured by BAM using XPS with an AXIS Ultra DLD (Kratos Analytical, Manchester, UK) using monochromatized Al Kα radiation in the hybrid lens mode. The effective attenuation length was determined traceably by comparison with XRR measurements at the PTB as reported in P190. Those of all the other films were measured by PTB using XRR at the four crystal monochromator beamline of the synchrotron radiation facility BESSY II at a photon energy of 8048 eV. The traceability to the SI unit meter is based on the X-ray wavelength of 0.1541 nm.

2) INMETRO

TEM measurements in INMETRO were carried out with a FEI Probe Corrected Titan 80-300 at 300 kV. The HRTEM images were acquired from at least 3 positions for every sample. Each lamella was aligned to the Si (110) zone axis of the substrate. The image was calibrated using the silicon atomic planes distances along the <1-11> crystalline direction as evaluated by FFT of TEM images and used as length reference.

3) KRISS

KRISS used MEIS for the thickness measurement of the HfO_2 films. MEIS measurements were carried out with a K-120 (K-Mac, Korea) using 100 kV He ion beams. Film thicknesses and uncertainties were traceably determined from the reference thicknesses and their standard uncertainties reported in P190.

4) NIM

In NIM, the thicknesses of the HfO_2 films were measured by XRR, XPS and TEM using X-ray diffractometer of type X'Pert PRO MRD (by Panalytical with Cu tube), Thermo Fisher Scientific Escalab 250Xi XPS system and ZEISS LIBRA 200 FE TEM, respectively. Among them, NIM submitted the thicknesses and uncertainties measured by XRR as the reference values of the key comparison. X-ray wavelength of XRR traced to SI unit through crystal lattice parameters of monocrystalline silicon, and angle of XRR traced to national angle standard through laser interferometer and autocollimator.

5) NIST

NIST used XRR with a nearly monochromatic source with an energy of 8.0478 ±0.0055 keV. Two X-ray diffraction (XRD) instruments from Rigaku SmartLabs (serial # HD2731N and JD2932N) were used. The film thicknesses of the four thick HfO_2 films (without the thinnest two films) were submitted as the key comparison values. The traceability to the SI unit meter is based on the X-ray wavelength.

6) NMIJ

In NMIJ, the thicknesses of HfO_2 films were evaluated by XPS and XRR. XPS analysis was carried out by a ESCA5800 (ULVAC-PHI, Japan) with monochromatic Al Kα radiation at the so-called reference geometry (at 34° from the surface normal in the azimuth at 22.5°). XRR measurements were carried out by a XRR system (Rigaku Corporation, Japan) with an X-ray generator (60 kV/ 300 mA) equipped with a Cu rotating anode. The thicknesses of the samples with the nominal thickness less than 3 nm (0.7, 1, and 2 nm) were determined by XPS and those of the other samples (3, 4, and 6 nm) were evaluated by XRR. The SI traceability of the thicknesses obtained by XPS in this study was realized by calibrating EAL with an SI-traceable XRR. Our SI-traceable XRR system is traceable to the SI for meter based on X-ray wavelength and the calibrated angle with a self-angle calibration system, which was demonstrated by comparing it with the Japanese national angle standard.

7) NMISA

NMISA determined the thicknesses of the HfO_2 layers using a Thermo ESCAlab 250Xi XPS instrument with a monochromatic Al Kα source. The measurements were carried out at the reference geometry, which is to say an emission angle θ of 34.0° and an azimuthal angle ϕ of 22.5°. The effective attenuation length L of 1.834 nm, as recommended by KRISS in the pilot study report, was used for traceability. R_0 was measured experimentally using pure Hf, SiO_2 and Si substrates.

8) NPL

At NPL, the thicknesses of HfO_2 films were measured by XPS and SE using mutual calibration. XPS analysis was carried out by a AXIS Ultra DLD (Kratos Analytical Ltd, UK) with a monochromated Al Kα X-ray source at the reference geometry (emission angle θ = 34.0° ± 1.0°, azimuthal angle ϕ = 22.5° ± 1.0°). SE data were acquired using a Woollam M-2000DI spectroscopic ellipsometer (wavelength range ~192 nm to 1700 nm). The instrument was calibrated using the manufacturer's fine calibration procedure. Uncertainty-weighted mean thicknesses for calibrated XPS and SE are reported, except for the thickest (nominal 6 nm) film for which only the offset-corrected SE result is reported. Thickness measurements are traceable to the wavelength of light through the ellipsometry analysis.

5. Measurement Results

The reported thickness values (d_i) of six HfO_2 films in K157 are listed in Table 2. The expanded uncertainties (U_i) were evaluated at 95% confidence level.

Table 2. Reported thickness values (d_i) of six HfO_2 films in this key comparison K157.

Thickness	0.7 nm		1 nm		2 nm		3 nm		4 nm		6 nm	
	d_i(nm)	U_i(nm)	d_i(nm)	U_i(nm)	d_i(nm)	U_i(nm)	d_i(nm)	U_i(nm)	d_i(nm)	U_i(nm)	d_i(nm)	U_i(nm)
BAM	**0.74**	0.13	**0.93**	0.16	-	-	-	-	-	-	-	-
PTB	**-**	-	**-**	-	**2.11**	0.08	**3.16**	0.12	**4.18**	0.14	**6.22**	0.14
INMETRO	**0.99**	0.64	**0.98**	0.62	**2.84**	0.71	**4.11**	0.63	**5.12**	0.71	**6.56**	0.75
KRISS	**0.73**	0.09	**1.06**	0.09	**2.16**	0.10	**3.13**	0.12	**4.29**	0.14	**6.13**	0.18
NIM	**0.78**	0.18	**1.11**	0.12	**2.12**	0.12	**3.22**	0.12	**4.21**	0.12	**6.20**	0.12
NIST	**-**	-	**-**	-	**2.12**	0.30	**3.14**	0.32	**4.22**	0.34	**6.14**	0.34
NMIJ	**0.66**	0.05	**1.03**	0.07	**2.20**	0.13	**3.30**	0.13	**4.26**	0.13	**6.34**	0.13
NMISA	**0.69**	0.08	**1.03**	0.11	**2.16**	0.19	**3.04**	0.23	**4.13**	0.28	**6.01**	0.36
NPL	**0.70**	0.05	**1.07**	0.07	**2.23**	0.11	**3.32**	0.14	**4.52**	0.15	**(6.68)***	(0.15)*

* This value by SE was treated as an outlier and was excluded from the calculation of the KCRV.

6. Key Comparison Reference Value and Uncertainty

The key comparison reference values (KCRV: d_R) and their standard uncertainties (u_R) of K157 were calculated by uncertainty-weighted mean method and corrected for observed dispersion.

$$d_R = \sum_{i=1}^{m} w_i d_i \quad \text{------------------------------} \quad (1)$$

$$w_i = \frac{u_i^{-2}}{\sum_{j=1}^{m} u_j^{-2}} \quad \text{------------------------------} \quad (2)$$

$$u_R = \sqrt{\frac{\chi_{obs}^2}{m-1}\left(\frac{1}{\sum_{i=1}^{m} u_i^{-2}}\right)} \quad \text{------------------------------} \quad (3)$$

$$\chi_{obs}^2 = \sum_{i=1}^{m} \frac{(d_i - d_R)^2}{u_i^2} \quad \text{------------------------------} \quad (4)$$

$$U_R = 2\, u_R \quad \text{------------------------------} \quad (5)$$

The key comparison reference values and the uncertainties of six HfO_2 films in CCQM-K157 are shown in Table 3. Figure 1 shows the reported average thicknesses (d_i) and the expanded uncertainties (U_{Ri}) of six HfO_2 films in K157. The solid blue lines and the broken red lines are the key comparison reference values and their uncertainties.

Table 3. Key comparison reference values and uncertainties of six HfO_2 films in K157.

Thickness	0.7 nm		1 nm		2 nm		3 nm		4 nm		6 nm	
	d_R (nm)	U_R (nm)	d_R (nm)	U_R (nm)	d_R (nm)	U_R (nm)	d_R (nm)	U_R (nm)	d_R (nm)	U_R (nm)	d_R (nm)	U_R (nm)
KCRV	**0.693**	0.026	**1.048**	0.031	**2.157**	0.047	**3.213**	0.084	**4.278**	0.099	**6.225**	0.066

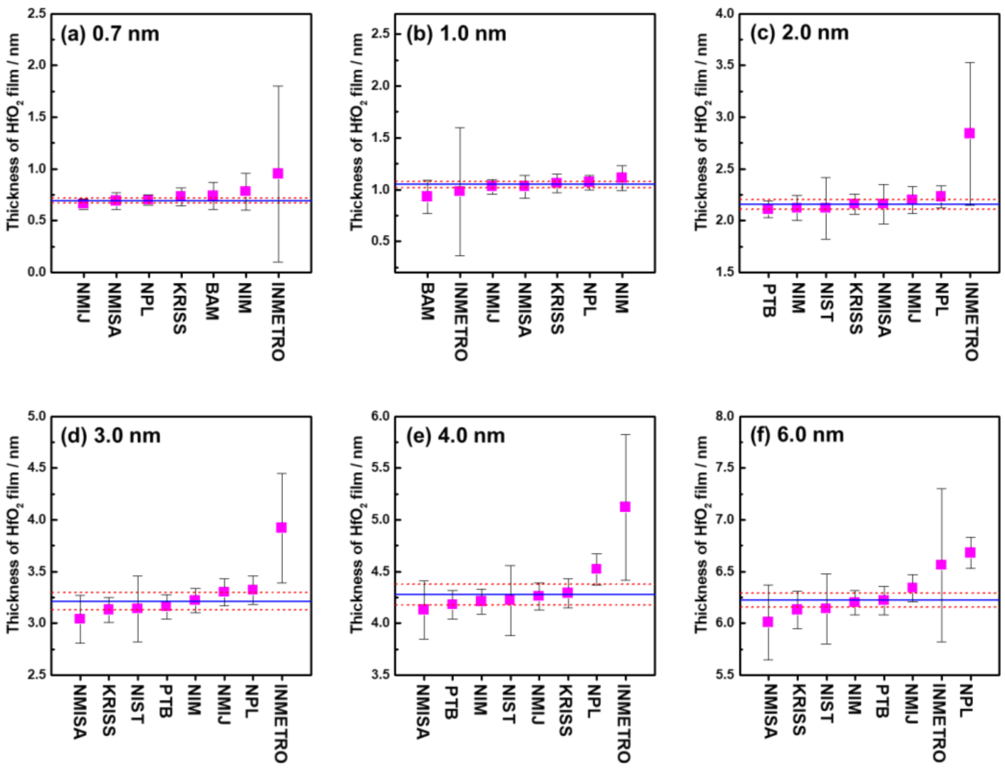

Figure 1. Key comparison reference values and their uncertainties in CCQM-K157 for six HfO_2 films. The solid blue lines and the broken red lines are the key comparison reference values and their standard uncertainties.

In the case of INMETRO, most of the data are deviated from the KCRVs because the offset value of TEM was not corrected. As reported in the pilot study P38 for the thickness measurement of SiO_2 films on Si(100), the offset value of TEM was about 0.8 nm. In the case of NPL, the thicknesses of the two thick films (4.0 and 6.0 nm) measured by spectroscopic ellipsometry (SE) are deviated from the KCRVs because SE was not calibrated from the reference thiknesses in P190.

7. Equivalence Statements

The equivalence statements were calculated for the participated eight laboratories from BIPM guidelines. The degrees of equivalence (D_i) of the reported results, d_i, and the KCRV, d_R, were calculated using the following expression:

$$D_i = d_i - d_R \text{ --- (6)}$$

The uncertainty for the degree of equivalence [$U(D_i)$] was calculated from the combination of the uncertainties of the individual data (U_i) and the uncertainty of the KCRV (U_R) from the following equation:

$$U^2(D_i) = U_i^2 + U_R^2 \text{ --- (7)}$$

8. Traceability for CMC

In CCQM pilot study P190, the traceability of thickness measurement of nm HfO_2 films was probed from the reference thicknesses determined by mutual calibration between x-ray reflectometry (XRR) and medium energy ion scattering spectrometry (MEIS). In the mutual calibration method, the traceability of thickness measurement of nm HfO_2 films was based on XRR as a length-unit traceable method from the wavelength of the used x-ray. In K157, the used instruments could be calibrated from the reference thicknesses and the participated NMIs may claim a CMC from the submitted K157 results and the KCRVs. Table 4 and Figure 2 show the degrees of equivalence (DoE) and their uncertainties for K157.

Table 4. Degrees of equivalence (DoE) and their uncertainties for K157.

Laboratory	0.7 nm		1 nm		2 nm		3 nm		4 nm		6 nm	
	D_i	$U(D_i)$	D_i	$U(D_i)$	D_i	$U(D_i)$	D_i	$U(D_i)$	D_i	$U(D_i)$	D_i	$U(D_i)$
BAM	0.047	0.133	-0.118	0.163	-	-	-	-	-	-	-	-
PTB	-	-	-	-	-0.047	0.093	-0.053	0.146	-0.098	0.171	-0.005	0.155
INMETRO	0.297	0.641	-0.068	0.621	0.683	0.712	0.897	0.636	0.842	0.717	0.335	0.753
KRISS	0.037	0.094	0.012	0.095	0.003	0.110	-0.083	0.146	0.012	0.171	-0.095	0.192
NIM	0.087	0.182	0.062	0.124	-0.037	0.129	0.007	0.146	-0.068	0.156	-0.025	0.137
NIST	-	-	-	-	-0.037	0.304	-0.073	0.331	-0.058	0.354	-0.085	0.346
NMIJ	-0.033	0.056	-0.018	0.077	0.043	0.138	0.087	0.155	-0.018	0.163	0.115	0.146
NMISA	-0.003	0.084	-0.018	0.114	0.003	0.196	-0.173	0.245	-0.148	0.297	-0.215	0.366
NPL	0.007	0.056	0.022	0.077	0.073	0.120	0.107	0.163	0.242	0.180	0.455	0.164

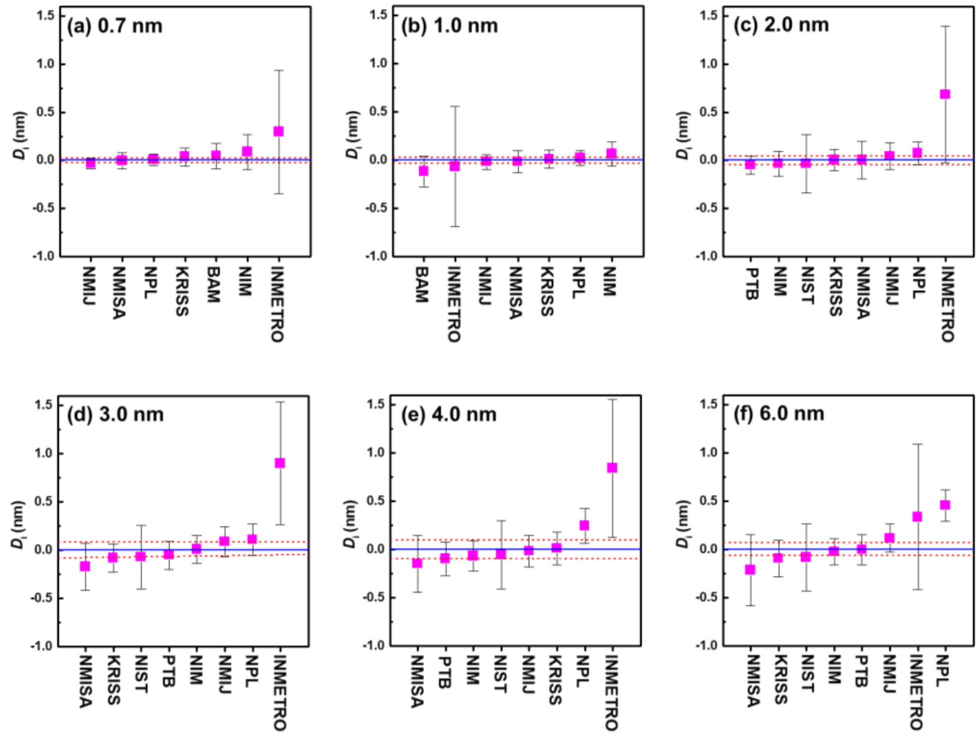

Figure 2. Degrees of equivalence (DoE) and their uncertainties for K157.

9. How far the light shines

This key comparison supports the CMC claims for the thickness measurement of HfO_2 films in the thickness range from 1 nm to 6 nm. This comparison can be a representative example for the thickness measurement of ultra-thin HfO_2 films by surface analysis methods.

10. Conclusion

CCQM key comparison K157 for thickness measurement of nm HfO_2 films was performed by the CCQM SAWG. The thicknesses of nm HfO_2 films were measured and reported by 8 NMIs and 1 DI using XPS, XRR, TEM, SE and MEIS. Nine laboratories reported the thicknesses of nm HfO_2 films within the due date and their results were compared to each other. The expanded uncertainties of the KCRVs for the HfO_2 films with nominal thickness from 0.7 nm to 6.0 nm were in the range from 0.026 nm to 0.099 nm, respectively.

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