Traceable thickness measurement of ultra-thin HfO$_2$ films by medium-energy ion scattering spectroscopy

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Abstract

The thicknesses of a series of ultra-thin HfO$_2$ films were precisely determined by mutual calibration by x-ray photoelectron spectroscopy (XPS) and x-ray reflectometry (XRR) in the recent Consultative Committee for Amount of Substance (CCQM) pilot study P-190. From these well-defined reference film thicknesses, the measurement capability of medium-energy ion scattering spectroscopy (MEIS) for the thickness of HfO$_2$ films was investigated. The film thicknesses determined by MEIS showed a small difference, within 2%, from the reference thicknesses and an offset value of 0.017 nm. The MEIS thicknesses can also be determined by mutual calibration between the transmission electron microscopy (TEM) thicknesses and the MEIS intensity ratios in the region of the substrate and HfO$_2$ film. From linear fitting with the reference thicknesses, the MEIS thicknesses determined by mutual calibration showed a slope value of 1.011 and an offset value of 0.015 nm. As a result, MEIS can be a traceable method to determine the absolute thickness of ultra-thin HfO$_2$ films, and a zero-offset method for application of the mutual calibration method.

Keywords: medium-energy ion scattering (MEIS), ultra-thin, oxide film, mutual calibration, thickness measurement

(Some figures may appear in colour only in the online journal)

1. Introduction

The thickness measurement of ultra-thin oxide films is very important for the development of semiconductor devices. For this reason, the thickness measurement of nanometer SiO$_2$ films was chosen as the first subject of the Consultative Committee for Amount of Substance (CCQM) Surface Analysis Working Group (SAWG) [1–5]. In the first pilot study, P-38, many kinds of thickness measurement methods were compared for thickness measurements of nanometer SiO$_2$ films on Si substrates. There were large offset values in a range from 0.5 nm to 1.0 nm in spectroscopic ellipsometry

(SE), transmission electron microscopy (TEM), Rutherford backscattering spectroscopy (RBS), nuclear reaction analysis (NRA), medium-energy ion scattering spectroscopy (MEIS) and x-ray reflectometry (XRR) [2]. These offset values are too large to accept because the thickness measurement range is only a few nanometers. As a result, it was found that the absolute thickness of ultra-thin oxide films is very difficult to determine using an individual surface analysis method.

Fortunately, however, the offset value of x-ray photoelectron spectroscopy (XPS) was found to be zero [6, 7]. This is because thickness measurement by XPS is determined from the relative ratio of the signal intensities of the constituent elements in the film and the substrate materials. That is, if the oxide thickness is close to 0, the peak area of the oxide

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component should be 0. The fact that the offset value of XPS is zero provided an opportunity to design a mutual calibration method to determine the absolute thickness of nanometer oxide films [8]. The mutual calibration method combines the strong points of a zero-offset method (such as XPS) and a length-unit traceable method (such as TEM). The mutual calibration method using XPS and TEM was applied to thickness measurements of SiO_2 [8], Al_2O_3 [9], and HfO_2 films [10].

HfO_2 is a dielectric material that can be used as an alternative to SiO_2. Therefore, a traceable thickness measurement of ultra-thin HfO_2 films, using physical or chemical methods, is required for advanced semiconductor industries. Thickness measurement of nanometer HfO_2 films was investigated as a recent subject of the pilot study P-190 by the CCQM SAWG. In P-190, the certified reference thicknesses of six HfO_2 films were determined by mutual calibration between the average thicknesses by XPS and XRR [11].

MEIS is known to be an excellent method to determine the amount of substance of ultra-thin films [12–14]. In this study, MEIS was investigated as a zero-offset method for application of the mutual calibration method, and suggested as a traceable method to determine the absolute thickness of ultra-thin HfO_2 films.

2. Experimental

2.1. Fabrication of samples

A series of $HfO_2/SiO_2/Si(100)$ films were fabricated for certification of thickness by mutual calibration with a length-unit traceable method and a zero-offset method. Six HfO_2 films with nominal thicknesses of 1.0 nm, 1.5 nm, 2.0 nm, 2.5 nm, 3.0 nm, and 4.0 nm were grown on the polished side of Si(100) substrates by atomic layer deposition. Before the growth of the HfO_2 films, to prevent the diffusion of oxygen atoms from the HfO_2 films to Si(100) substrate, 2 nm SiO_2 layers were grown on the Si(100) substrates by thermal oxidation, as shown in figure 3. After growth of the HfO_2 films, the wafers were cut into small specimens with sizes of 10 mm × 10 mm.

2.2. Determination of reference thickness

To investigate the traceability of thickness measurement, the determination of well-defined film thicknesses is an important prerequisite. The reference thicknesses of the HfO_2 layers in a series of $HfO_2/SiO_2/Si(100)$ films were determined by mutual calibration between the average thicknesses by XPS and XRR reported in the pilot study P-190 by 11 national metrology institutes. The linear fitting line showed the good linear relationship between the two average thicknesses of the XPS and XRR. The reference thicknesses were determined from the average values of the XPS thicknesses corrected by the slope, and the XRR thicknesses corrected by the offset value of the linear fitting line. These reference thicknesses can be regarded as traceable values because they are based on the thickness obtained by XRR, where the thickness scale is based on the wavelength of x-rays.
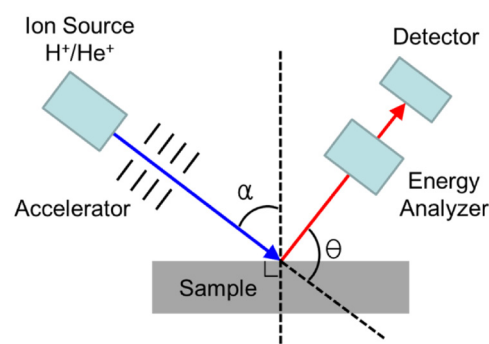

Figure 1. A schematic diagram of a typical MEIS system. The incident angle is α, and the scattering angle is θ.
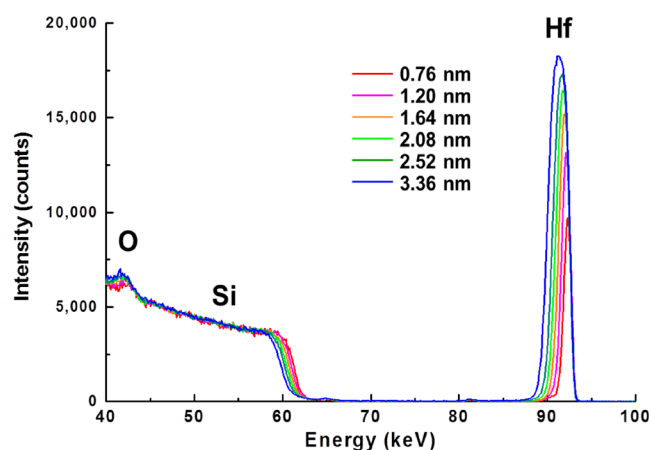

Figure 2. MEIS spectra of a series of $HfO_2/SiO_2/Si(100)$ films used in the pilot study P-190.

2.3. TEM analysis

Thicknesses of HfO_2 films were determined from high-resolution (HR) TEM micrographs collected using FEI-F30 microscopes operating at 300 kV. The film thicknesses of the samples were determined from the lattice constant of the Si(100) substrate. The HfO_2/SiO_2 interface was determined from the point with half of the average contrast of the SiO_2 layer and that of the HfO_2 layer. More than ten TEM images at different locations were obtained.

2.4. MEIS analysis

Thickness of the HfO_2 films was measured using an MEIS system (K-120, K-MAC, Korea), which consists of an ion source, an accelerator, an energy analyser, and a detector, as schematically shown in figure 1. The incident and scattering angles are determined by the geometric arrangement between the ion source, the sample, and the detector. In MEIS analysis, ions generated from an ion source are accelerated to impinge on the sample surface, and the energy of the ions scattered by the nuclei of the constituent atoms is measured by an energy analyser. From the energy distribution of scattered ions, the in-depth locations of the constituent atoms can be determined from kinematic factors, and the quantity of atoms can also be determined from the scattering cross section of the atoms. An electrostatic analyser, magnetic sector analyser, and time of
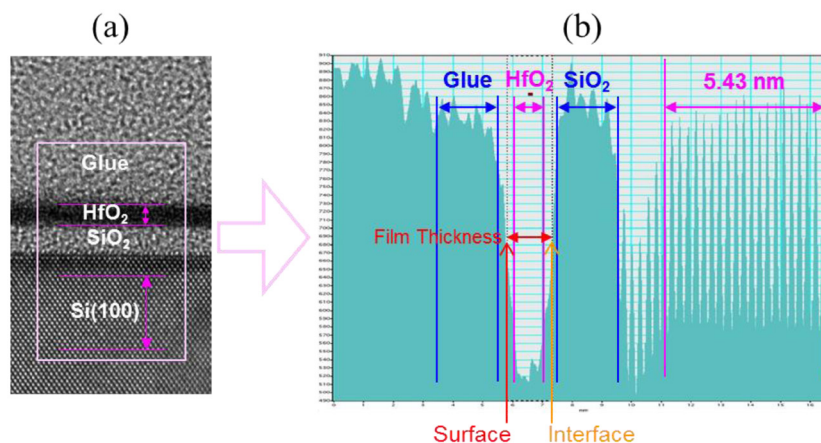
Figure 3. An HR-TEM image (a) and an intensity profile image (b) of HfO$_2$ (1.5 nm)/SiO$_2$(2.0 nm)/Si(1 0 0) film.

flight (TOF) analyser are widely used for MEIS analysis. Of these, the TOF analyser, because it is the most quantitative, is robust for thickness measurement of ultra-thin oxide films. The TOF analyser acquires scattered particles, both charged and neutralized, and so neutralization correction is not needed in the analysis; therefore, there is no potential error in the charge correction. In addition to this, a full energy spectrum is always obtained, which provides a perfect internal reference.

3. Results and discussion

In this study, to investigate the measurement capability of the MEIS system, the thicknesses of a series of HfO$_2$/SiO$_2$/Si(1 0 0) films used in the pilot study P-190 were measured by MEIS and HR-TEM, as shown in figure 2. In the measurement, He$^+$ ions with a voltage of 100 keV were used. The incident angle was 45°, and the scattering angle was 130°. The pulse width of the ion beam was 350 ps. The ion beam current was about 100 pA, as monitored *in situ* during the experiment using a Faraday cup installed in the middle of the ion beam column. The ion dose on the sample was kept at 500 nC by controlling the irradiation time, which was calculated based on the ion beam current. The sample was continuously rotated around the normal axis of the surface to ensure random spectrum measurement. The detector open area for the data acquisition was confined to $\Delta\theta = 5°$ and $\Delta\phi = 5°$.

The signal intensity of crystalline Si is very reproducible within the relative standard deviation of 0.54%. On the other hand, Hf peaks show a gradual increase proportional to the reference thicknesses described in figure 2.

3.1. Thickness measurement by HR-TEM

Because its scale is based on the lattice constant, HR-TEM is a length-unit traceable thickness measurement method. In particular, in thin films grown on Si(1 0 0) wafers, the crystalline lattice planes of Si can be directly used as an internal standard to measure the absolute film thickness. The lattice distance between Si(1 1 0) planes in the cross-sectional TEM image is 0.543 nm.

An HR-TEM image of an HfO$_2$/SiO$_2$/Si(1 0 0) film can be simply converted to an intensity line profile image using the average contrast of the region of interest (ROI), as shown in figure 3. For precise measurement, the aspect ratio of the lattice line should be maximized by aligning the lines parallel to the lattice direction, and as such, parallel to the interface and film surface.

The locations of the interface and the surface at which the film thickness is measured can be determined from the contrast profile. The location of the SiO$_2$/HfO$_2$ interface can be determined from the point of half contrast between the average contrast of the SiO$_2$ (I_{SiO_2}) and HfO$_2$ (I_{HfO_2}) layers, $(I_{SiO_2} + I_{HfO_2})/2$. In the same manner, the location of the film's surface can be determined from the average contrast of the HfO$_2$ (I_{HfO_2}) and the glue (I_{glue}) layers using the relation $(I_{glue} + I_{HfO_2})/2$.

The film thickness can be measured from the distance between the SiO$_2$/HfO$_2$ interface and the surface of the HfO$_2$ layer. The thickness of the HfO$_2$ layer can be simply determined from the ratio of the line width of the HfO$_2$ layer and the width of 20 lines of Si(1 0 0) planes corresponding to the value of 5.431 nm for ten Si lattice constants [15–17]. The average TEM thicknesses of the HfO$_2$ films (T_{TEM}), derived from more than ten TEM images at different locations, are shown in table 1.

The combined standard uncertainty (u_c) is calculated from the equation $u_c^2 = u_m^2 + u_d^2 + u_r^2 + u_l^2$. Here, u_m is the standard uncertainty in the measurement of film thickness, and u_d is the standard uncertainty in the definition of the interface and surface, which is related to the offset value of the TEM. It was reported in the range of (0.1–0.2) nm [8–10]. In this study, a small value of 0.1 nm was assigned as the value of u_d. Here, u_r is the standard uncertainty in the measurement of the line width of the periodic Si(1 0 0) lattice planes. It is the uncertainty in the measurement of the interval of the periodic 20 Si(1 0 0) lattice planes, as shown in figure 3(b). The u_r value was measured to be small to be 0.01 nm. Here, u_l is the standard uncertainty of the variation of the Si lattice constant; u_l is negligibly small to be 0.89×10^{-8} nm [15]. The expanded uncertainty (U) was determined from the equation $U = Ku_c$ at a 95% confidence level.

Table 1. Thicknesses of HfO$_2$ films determined by HR-TEM (T_{TEM}).

Number of specimen	Measured thickness (nm)	Uncertainty parameters (nm)				Expanded uncertainty U (nm)
		u_{m}	u_{d}	u_{r}	u_{l}	
1	1.25	0.03	0.100	0.01	0.00	0.21
2	1.60	0.02	0.100	0.01	0.00	0.20
3	2.11	0.02	0.100	0.01	0.00	0.21
4	2.57	0.05	0.100	0.01	0.00	0.22
5	3.03	0.03	0.100	0.01	0.00	0.21
6	3.76	0.02	0.100	0.01	0.00	0.21

Table 2. The number of Hf atoms and thicknesses of HfO$_2$/SiO$_2$/Si(100) films measured by MEIS.

Number of Hf atoms (1×10^{15} atoms cm^{-2})			MEIS thickness (nm)			T_{MEIS} (nm)	Stdev (nm)	RSD (%)
1	2	3	1	2	3			
2.14	2.11	2.12	0.773	0.762	0.764	0.766	0.006	0.765
3.35	3.38	3.38	1.208	1.221	1.221	1.217	0.008	0.617
4.60	4.54	4.54	1.660	1.640	1.640	1.647	0.012	0.701
5.79	5.81	5.78	2.092	2.099	2.086	2.092	0.007	0.311
7.04	7.01	6.98	2.541	2.531	2.520	2.531	0.011	0.415
9.44	9.48	9.55	3.410	3.425	3.450	3.428	0.020	0.589

3.2. Thickness measurement by MEIS

In MEIS analysis, the thickness of the HfO$_2$ films can be determined from the measured number of constituent Hf atoms within a unit area and the number density of the bulk HfO$_2$. The number of the constituent Hf atoms is measured by simulation of the obtained MEIS spectrum. MEIS is a program developed at K-MAC and used as a simulation tool for MEIS spectra analysis. In the analysis, the Andersen cross section [18] and Chu straggling [19] were used. For the stopping power, fitted values based on the experimental data [20] were used following recent MEIS round robin test results [21]. The simulations took into account the solid angle of the detector, and the kinematic broadening of each element was reliably applied. Multiple scattering effects were included in the calculation.

The thickness of the HfO$_2$ films (T_{MEIS}) can be determined by dividing the measured number of Hf atoms in the unit area (atoms cm^{-2}) by the number density of the bulk HfO$_2$ ($=8.32 \times 10^{22}$ atoms cm^{-3}). The number of Hf atoms was measured three times by MEIS. The number of Hf atoms and the thicknesses of HfO$_2$/SiO$_2$/Si(100) films derived from the number of Hf atoms are shown in table 2. The linear fitting results of the measured thickness compared to the reference thicknesses show a slope value of 0.981 and an offset value of 0.017 nm. The slope value of 0.981 means that the measured MEIS thicknesses of the HfO$_2$ films are close to the reference thicknesses, within 2%.

3.3. Thickness measurement by mutual calibration

Mutual calibration using a combination of a zero-offset method and a length-unit traceable method was suggested as a useful method to determine the absolute thickness of ultra-thin oxide films. MEIS can be used as a zero-offset method
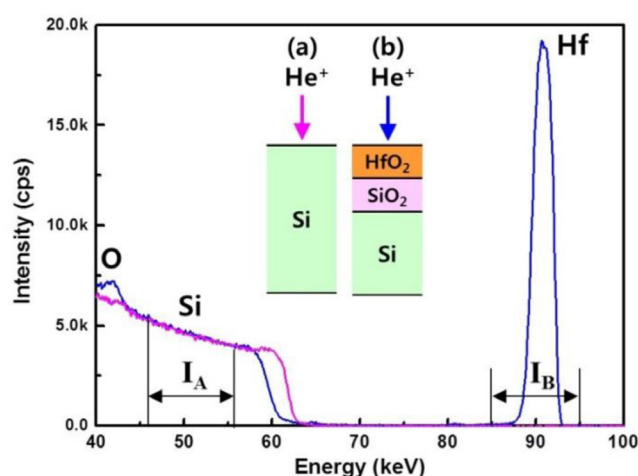

Figure 4. MEIS spectra of (a) Si(100) substrate without film (magenta) and (b) HfO$_2$/SiO$_2$/Si(100) film (blue).

in the mutual calibration method because the film thickness depends on the number of atoms in the oxide film according to the basis of the number density of c-Si. In this study, the thickness of nanometer HfO$_2$ films was directly measured by the mutual calibration method from the MEIS spectra and the thicknesses measured by HR-TEM shown in table 1.

In MEIS, the number of scattered ions is related to the scattering cross section of the constituent atoms. In the thickness measurement of an HfO$_2$ thin film grown on crystalline Si substrate, the signal intensity of the substrate can be a basis for thickness measurement because the number density of crystalline Si is a constant. Figure 4 shows the MEIS spectra of Si(100) substrate (magenta) without film and HfO$_2$/SiO$_2$/Si(100) film (blue). The fact that the intensities of Si are identical in the substrate without film and in the ultra-thin HfO$_2$/SiO$_2$/Si(100) film is the basis for the thickness measurement.

Table 3. MEIS intensities of substrate (I_A) and HfO$_2$ HfO$_2$/SiO$_2$/Si(1 0 0) films (I_B) and their ratios ($R = I_B/I_A$) determined from three MEIS spectra.

| Measurement		1	2	3	4	5	6
1	I_A	456 211	456 813	457 875	458 174	459 707	462 033
	I_B	111 006	175 448	239 460	303 839	369 497	500 151
	$R = I_B/I_A$	0.2433	0.3841	0.5230	0.6632	0.8038	1.0825
2	I_A	456 968	455 821	457 874	458 486	458 420	461 614
	I_B	111 259	175 679	238 932	303 589	368 062	500 280
	$R = I_B/I_A$	0.2435	0.3854	0.5218	0.6622	0.8029	1.0838
3	I_A	457 262	456 454	458 058	457 814	459 414	461 386
	I_B	111 185	176 238	238 702	303 155	367 120	502 713
	$R = I_B/I_A$	0.2432	0.3861	0.5211	0.6622	0.7991	1.0896
Average of R		0.2433	0.3852	0.5220	0.6625	0.8019	1.0853
Stdev of R		0.0002	0.0010	0.0009	0.0006	0.0025	0.0038
RSD of R (%)		0.07	0.27	0.18	0.09	0.31	0.35
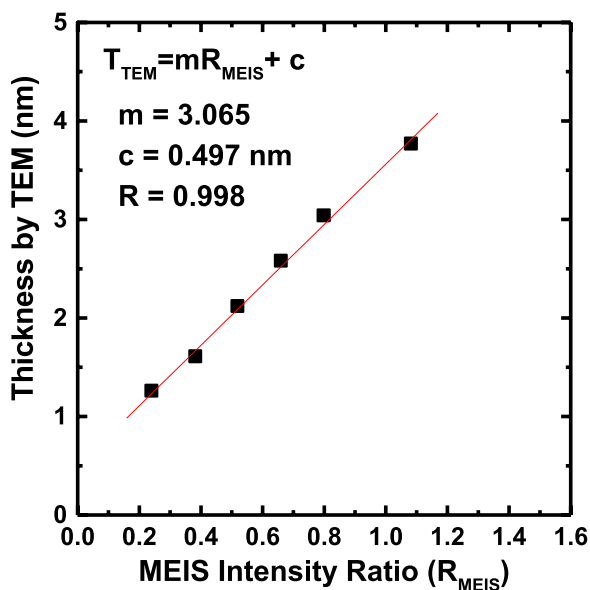
Figure 5. The mutual calibration result of the MEIS intensity ratio (R_{MEIS}) and average TEM thicknesses (T_{TEM}).

For this reason, the relative intensity ratio ($R_{MEIS} = I_B/I_A$) of film material (B) to substrate (A) can be converted to the thickness (T_{MEIS}) of the HfO$_2$ layer. The proportional factor can be determined from the slope, derived from mutual calibration by MEIS, a zero-offset method, and HR-TEM, a length-unit traceable method. The intensities of the crystalline Si substrate (I_A) were determined to be in the energy range from 46 keV to 56 keV from the MEIS spectra shown in figure 4. The intensities of Hf in the six HfO$_2$ films (I_B) were also determined to be in the energy range from 85 keV to 95 keV. Table 3 shows the MEIS intensities of the substrate (I_A) and of the HfO$_2$/SiO$_2$/Si(1 0 0) films (I_B), and their ratios ($R = I_B/I_A$) determined from the three MEIS spectra.

The variations in the values of the signal intensities of the crystalline Si substrate show very small relative standard deviations of 0.46%, 0.43%, and 0.38%. The signal intensities of the Hf peaks show a gradual increase proportional to the reference thicknesses. The variations in the values of the signal intensity ratios ($R = I_B/I_A$) in the three MEIS spectra of the HfO$_2$/SiO$_2$/Si(1 0 0) films are also very small at 0.07%,

Table 4. Reference thicknesses and certified thicknesses of HfO$_2$ films determined by mutual calibration with MEIS and TEM.

Reference thickness (nm)	Thickness (nm)		Certified thickness (nm)	
T_{Ref}	R_{MEIS}	T_{TEM}	T_{MEIS}^C	T_{TEM}^C
0.76	0.24	1.25	0.74	0.75
1.20	0.39	1.60	1.18	1.10
1.64	0.52	2.11	1.60	1.61
2.08	0.66	2.57	2.03	2.07
2.52	0.80	3.03	2.46	2.53
3.36	1.09	3.76	3.33	3.26
slope	3.099	1.008	1.011	1.008
offset	0.015	−0.479	0.015	0.025
R	1.000	0.999	1.000	0.999
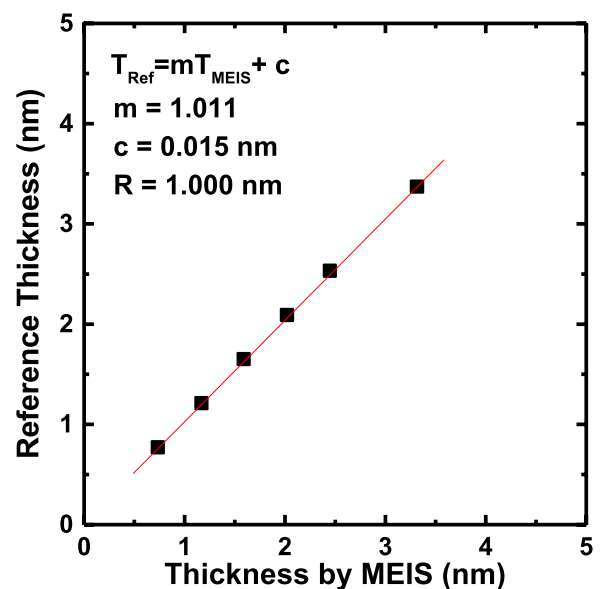
Figure 6. Linear fitting of MEIS thicknesses (T_{MEIS}) and reference thicknesses (T_{Ref}).

0.27%, 0.18%, 0.09%, 0.31%, and 0.35%. These reproducible results can be a basis for traceable thickness measurement of ultra-thin oxide films.

In this study, the relative intensity ratios ($R_{MEIS} = I_B/I_A$) of the film material (B) and substrate (A) were converted to thicknesses. The MEIS thicknesses (T_{MEIS}) of the HfO_2 films can be determined by mutual calibration from the average relative intensity ratio ($R_{MEIS} = I_B/I_A$), shown in table 3, and the traceable thicknesses by TEM (T_{TEM}), shown in table 1. Figure 5 shows the mutual calibration results of the MEIS intensity ratio (R_{MEIS}) and the average TEM thicknesses (T_{TEM}). The MEIS intensity ratios are very linearly proportional to the average TEM thicknesses.

The slope *m* and offset values *c* are key parameters for the determination of the film thickness by mutual calibration. The measured value of *m* is 3.065 ± 0.097; the measured value of *c* is $0.497\,nm \pm 0.066\,nm$. From the slope and offset values, the certified MEIS thicknesses (T_{MEIS}^C) and TEM thicknesses (T_{TEM}^C) can be determined as follows:

$$T_{MEIS}^C = R_{MEIS} \times 3.065\,nm$$

$$T_{TEM}^C = T_{TEM} - 0.497\,nm.$$

Table 4 shows the certified MEIS thicknesses (T_{MEIS}^C) and TEM thicknesses (T_{TEM}^C) together with the measured raw thicknesses and the reference thicknesses. The slope and the offset values were derived from linear fitting of the measured and certified thicknesses by MEIS and TEM to the reference thicknesses. The MEIS thicknesses can be used as certified values because the length scale was calibrated from TEM based on the lattice constant of crystalline Si substrate.

Figure 6 shows the linear fitting results of the MEIS thicknesses (T_{MEIS}) and the reference thicknesses (T_{Ref}). The slope value (1.011) close to unity means the MEIS thicknesses are identical to the reference thicknesses, within 1.1%. The small offset value of 0.015 nm also means that the MEIS thicknesses are close to the reference thicknesses from P-190 performed by national metrology institutes (NMIs). It means that the role of MEIS as a zero-offset method can be said to be comparable to the role of average XPS thickness in P-190 within the uncertainty level.

4. Conclusion

To investigate the measurement capability of the MEIS system, the thickness of HfO_2 layers in a series of $HfO_2/SiO_2/Si(1\,0\,0)$ films was measured by MEIS. The MEIS thicknesses determined by simulation showed a difference of about 2% from the reference thicknesses and the offset value of 0.017 nm. The MEIS thicknesses can be determined without simulation by mutual calibration between the TEM thicknesses and the MEIS intensity ratios in the region of the substrate and HfO_2

film. The MEIS thicknesses obtained by mutual calibration showed a slope value of 1.011 and offset value of 0.015 nm in linear fitting with the reference thicknesses. MEIS can be used as a traceable method to determine the absolute thickness of ultra-thin oxide films and a zero-offset method for application of the mutual calibration method.

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