Thickness Measurement of Ultra-thin TiO₂ Films by Mutual Calibration Method

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ABSTRACT

Mutual calibration with length-unit traceable and zero-offset methods has been recently suggested as a reliable method to determine the absolute thickness of the ultra-thin oxide films. In this study, the thickness of the TiO₂ film on Si (100) substrate was determined using the mutual calibration method. A series of ultra-thin TiO₂ films were fabricated via atomic layer deposition. The thicknesses of the TiO₂ films were measured by X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and medium energy ion scattering spectroscopy (MEIS). The absolute thickness was determined by mutual calibration using a combination of high-resolution (HR)-TEM and MEIS. The thickness was also measured by mutual calibration employing a combination of HR-TEM and XPS to compare the two zero-offset methods (XPS and MEIS). A large offset difference of 0.45 nm was observed between the two data. This was related to the difference in the escape depth of the photoelectrons from the film and substrate in XPS analysis due to the surface contamination layer.

Keywords: Thickness measurement, TiO₂, X-ray photoelectron spectroscopy, Transmission electron microscopy, Medium energy ion scattering spectroscopy, Mutual calibration method

1. Introduction

The thickness measurement of ultra-thin oxide films is an important metrology issue in the fabrication of next-generation electronic devices [1-3]. Although various kinds of thickness measurement methods such as spectroscopic ellipsometry (SE), x-ray reflection (XRR), transmission electron microscopy (TEM), Rutherford backscattering spectrometry (RBS) and medium energy ion scattering spectroscopy (MEIS) have been investigated, it has been reported that the absolute thickness of ultra-thin oxide films is difficult to measure due to the large offset values [4].

A mutual calibration method has been suggested as a method to solve the problem of the large offset values in the range of 0.5 ~ 1.0 nm. This is based on the combination of a length-unit traceable method (such as TEM and XRR) and a zero-offset method (such as X-ray photoelectron spectroscopy (XPS) and MEIS). The large offset values in TEM and XRR can be calibrated by the zero-offset methods and the thickness can be traceably calibrated by the length-unit traceable methods [1]. Thickness measurements of SiO₂ [1], Al₂O₃ [5], and HfO₂ [6] films by mutual calibration with XPS and TEM have been reported. Recently, thickness measurement of HfO₂ films by mutual calibration with MEIS and TEM was also reported [7].

Titanium dioxide (TiO₂) films have been widely used in the fields of solar cells [8], electronic devices and capacitors [9,10] because of their high dielectric and high band gap semiconductor ($E_g = 3.2$ eV) [11,12]. In this study, thickness measurement of ultra-thin TiO₂ films

grown by atomic layer deposition (ALD) was investigated. The film thickness could be precisely controlled in the ALD process by self-limiting [13-15].

MEIS is a unique method for the thickness measurement and quantitative depth profiling analysis of ultra-thin layers [16-18]. In this paper, the thicknesses of the TiO₂ films on Si (100) substrates were measured by TEM, XPS, and MEIS. The thicknesses of the TiO₂ films were determined by mutual calibration with MEIS and TEM. A large discrepancy in the offset values due to the surface contamination layer was observed in a comparison of the thicknesses measured by XPS and MEIS. Although XPS has been reported as a useful zero-offset method, the surface contamination layer should be well eliminated for the precise thickness measurement of ultra-thin oxide films.

2. Experimental

2.1. Fabrication of samples

A series of TiO₂ films were grown on a n-type single side polished Si (100) substrate by the atomic layer deposition method. Titanium (IV) isopropoxide (TTIP) and water (H₂O) were used as a precursor and a reactant, respectively. Five TiO₂/Si (100) films with different thickness were deposited using Atomic Shell (CN1, Korea). Prior to TiO₂ deposition, the Si (100) substrate was cleaned by a RCA solution [19] and the surface native oxide was eliminated by a diluted HF solution. The wafers were diced into small specimens with a size of

10 mm × 10 mm. The deposition temperature was set to 200 °C and the processing cycle consisted of a 0.3 s pulse of TTIP for TiO₂ deposition with a 15 s purge pulse of N₂ and a 0.3 s pulse of H₂O with a 15 s purge pulse of N₂. The thicknesses of the TiO₂ films were controlled by the deposition cycles of 20, 40, 60, 80, and 100 cycles, respectively.

2.2. Thickness measurement by TEM

HR-TEM can be a length-unit traceable method because the scale is based on the lattice constant of the crystalline Si substrate. Thicknesses of the ultra-thin TiO₂ films were determined from high resolution TEM (HR-TEM) using a JEM-ARM 200F microscope. The lattice constant of the crystalline Si substrate can be used as an internal standard for the measurement of the absolute film thickness, as shown in Fig. 1. The lattice constant (α) between the Si (100) lattice

Figure 1. HR-TEM image of a TiO₂/Si (100) specimen and the unit cell of the Si (100) substrate.

Figure 2. (a) High resolution TEM image, (b) contrast intensity profile, and (c) differential contrast intensity profile.

Figure 3. HR-TEM images of the five TiO₂/Si (100) films grown during (a) 20, (b) 40, (c) 60, (d) 80, and (e) 100 cycles.

planes in the cross-sectional TEM image is $5.431\,020\,511 \times 10^{-10}$ m, as given in NIST Reference on Constant, Units, and Uncertainty. The standard uncertainty of the lattice constant is $0.000\,000\,089 \times 10^{-10}$ m ($= 1.6 \times 10^{-8} \%$) [20].

The intensity line profile image can be obtained from the average contrast in the region of interest (ROI), as shown in Fig. 2. The lattice intensity can be maximized by aligning the Si (100) lattice lines parallel to the interface and the film surface. In this case, the distance of the two Si (100) lattice lines corresponds to the lattice constant $5.431\,020\,511 \times 10^{-10}$ m and the thickness of 20 Si (100) lattice lines is 5.431 nm.

In the intensity line profile, the locations of the interface and the surface to measure the film thickness can be determined by an average contrast (AC) method and an inflection point (IP) method. In the AC method, the location of the SiO₂/TiO₂ interface is determined from the point of half contrast ($(I_{\text{SiO}_2} + I_{\text{TiO}_2})/2$) between the average contrast of the SiO₂ (I_{SiO_2}) and TiO₂ (I_{TiO_2}) layers as shown in Fig. 2(b). In the same manner, the location of the film surface can be determined from the average contrast ($(I_{\text{glue}} + I_{\text{TiO}_2})/2$) of the TiO₂ (I_{TiO_2}) and the glue (I_{glue}) layers. The film thickness is determined from the distance between the interface of SiO₂/TiO₂ and that of TiO₂/glue.

In the IP method, the contrast intensity profile is smoothened first by averaging the intensities of the nearest eleven points. The film thickness is determined from the distance between the inflection points in the differential intensity line profile, as shown in Fig. 2(c). Here, the locations of the SiO₂/TiO₂ and TiO₂/glue interfaces to determine the thicknesses is determined at the minimum (F1) and maximum (F2) points in the differential profile, respectively [21].

Figure 3 shows the HR-TEM images of the five TiO₂/Si (100) films grown by ALD during 20, 40, 60, 80, and 100 cycles. Although the contrast difference between the native SiO₂ layer and the TiO₂ layer is large enough to distinguish them, the locations of the interfaces and surfaces are not easy to determine. For reliable thickness measurement of the films by TEM, more than five images were measured at different points.

2.3. Thickness measurement by XPS

The thicknesses of the TiO₂ films were measured by an XPS system (VersaProbe II, Ulvac-PHI, Japan) operated at the Al K α line of 1486.6 eV. Before loading the samples into the XPS chamber, the surface contamination layers of the TiO₂/Si (100) films were cleaned with isopropyl alcohol and acetone. Figure 4 shows the Ti 2p and Si 2p spectra of the TiO₂/Si (100) films. The thickness of the TiO₂ films (T_{TiO_2}) was determined by the following equation [4]:

$$T_{\text{TiO}_2} = L \cos \theta \ln(R_{\text{exp}}/R_0 + 1) \quad (1)$$

where L is the attenuation length of the photoelectrons from the films, θ is the electron emission angle from the surface normal, and R_0 ($= I_{\text{TiO}_2}^{\infty}/I_{\text{Si}}^{\infty}$) is the ratio of the intensities from the pure bulk material and the substrate material. $I_{\text{TiO}_2}^{\infty}$ and I_{Si}^{∞} were directly obtained from the peak areas of the Ti 2p and Si 2p peaks of a thick TiO₂ film and a cleaned Si(100) wafer, respectively.

R_{exp} ($= I_{\text{film}}^{\text{exp}}/I_{\text{sub}}^{\text{exp}}$) is the relative ratio of the peak intensities of the film layer ($I_{\text{film}}^{\text{exp}}$) and the substrate ($I_{\text{sub}}^{\text{exp}}$). The peak intensity of the film layer ($I_{\text{film}}^{\text{exp}}$) is simply obtained from the peak area of Ti 2p

Figure 4. Ti 2p and Si 2p XPS spectra of the TiO₂/Si (100) films.

from the measured XPS spectra of the TiO₂/Si (100) films. On the other hand, the peak intensity of the substrate (I_{sub}^{exp}) is somewhat complicated to determine because the interfacial SiO₂ layer is generally formed during the growth of oxide film on the Si (100) substrate. In this case, the oxide species should be included in the intensity of the substrate (I_{sub}^{exp}) by the following equation:

$$I_{sub}^{exp} = I_{SiO_2}^{exp} + I_{Si}^{exp} \times (I_{SiO_2}^{\infty} / I_{Si}^{\infty}) \quad (2)$$

The intensity ratio ($I_{Si}^{\infty} / I_{SiO_2}^{\infty}$) of pure Si and pure SiO₂ was reported to be 0.852. This value was used in this study. The signal intensities of I_{Si}^{exp} and $I_{SiO_2}^{exp}$ were determined from the Si 2p spectra of the TiO₂/Si (100) films from the following equations [6]:

$$I_{Si}^{exp} = Si^0 + 0.75 \times Si^{1+} + 0.5 \times Si^{2+} + 0.25 \times Si^{3+} \quad (3)$$

$$I_{SiO_2}^{exp} = Si^{4+} + 0.75 \times Si^{3+} + 0.5 \times Si^{2+} + 0.25 \times Si^{1+} \quad (4)$$

R_{exp} and R_0 should be determined from experimental measurement under the same experimental geometry and experimental conditions. In this study, the experimental values of R_0 and θ were 2.218 and 45°, respectively. The inelastic mean free path of 2.365 nm calculated by the TPP-2M equation [22,23] was used as the value of the electron attenuation length L .

2.4. Thickness measurement by MEIS

The thicknesses of the TiO₂ films were measured by a MEIS system (K-120, KMAC, Korea). He⁺ ion beam with a voltage of 100 keV was used at an incident angle and a scattering angle of 45° and 130°, respectively. In MEIS, the energy of the scattered He ions depends on the mass of the target elements and the scattering depth [16,24]. The number of the scattered ions is proportional to the number of constituent elements of the oxide layer from the scattering cross section. Therefore, if the composition of the elements is uniform with depth in the oxide layer, the thickness of the oxide layer will be related with the number of elements. In the thickness measurement of the TiO₂/Si (100) films by MEIS, the signal intensity of the substrate can be a basis for thickness measurement because the number density of the crystalline Si substrate is constant. Figure 5 shows the MEIS

Figure 5. MEIS spectra of the TiO₂ films on Si (100) substrate.

spectra of the TiO₂/Si (100) films. The thicknesses of the TiO₂/Si (100) films can be determined by the mutual calibration method. The relative intensity ratios ($R_{MEIS} = I_{Ti}/I_{Si}$) of the film material (I_{Ti}) to the substrate (I_{Si}) can be converted to the thicknesses (T_{MEIS}) of the TiO₂ films by the following equation:

$$T_{MEIS} = K \times R_{MEIS} \quad (K = m_{CM}) \quad (5)$$

Here, I_{Si} is determined by summation of the Si intensities in the energy period between 45 and 55 keV. I_{Ti} is determined by summation of the Ti intensities in the energy period between 68 and 78 keV.

The proportional factor (K) can be determined from the slope (m_{CM}) in a mutual calibration by linear fitting of the thicknesses by MEIS as a zero-offset method and the thicknesses by HR-TEM as a length-unit traceable method.

2.5. Mutual calibration method

For the thickness measurement of ultra-thin oxide films, a mutual calibration method (MCM) is based on the combination of a zero-offset method (ZOM) for the compensation of offset value and a length-unit traceable method (LTM) to calibrate the thickness scale from the SI length unit [1,7]. The measured thickness by a ZOM (such as XPS and MEIS) is converged to zero when the real thickness of the film is close to zero because the thickness depends on the amount of constituent elements of the film. However, the thickness scale of the measured thickness by ZOM is not traceable. The measured thickness by a LTM (such as TEM and XRR) is traceable because the thickness scale is based on the SI unit of physical length. However, the offset value may not be zero due to the incorrect determination of the locations of the interface and the surface of the film.

Calibration of the mismatch between the thicknesses measured by ZOM and LTM is the main function of the mutual calibration method. In the mutual calibration method, the offset value c and the slope value of m are derived from linear fitting of the thicknesses by ZOM and LTM by the following linear equation:

$$T_{LTM} = mT_{ZOM} + c \quad (6)$$

The offset value c means the excess thickness when the real thickness is close to zero and the slope m is the thickness scale of the

measured film thickness. The certified thickness (T^c) of the films can be determined from the calibrated thicknesses (T_{LTM}^c, T_{ZOM}^c) by the following relations [1]:

$$T_{LTM}^c = T_{LTM} - c \quad (7)$$

$$T_{ZOM}^c = m T_{ZOM} \quad (8)$$

$$T^c = T_{LTM}^c + T_{ZOM}^c / 2 \quad (9)$$

3. Discussion

3.1. Absolute film thickness by MCM with MEIS and TEM

A mutual calibration method with a combination of MEIS and TEM has been reported as a measurement method to determine the absolute thickness of ultra-thin oxide films [7]. In this study, the absolute thicknesses of the TiO₂/Si (100) films were determined by mutual calibration of MEIS and TEM. Table I shows the average thicknesses measured from TEM and the MEIS intensity ratios $R (= I_{Ti} / I_{Si})$. Figure 6 shows a linear plot between the thicknesses by TEM and the MEIS intensity ratios. The thicknesses by TEM determined by the inflection point (IP) method were used. As the result of the linear fit,

Table I. MEIS intensity ratios of TiO₂ films and thicknesses by TEM with IP and AC methods.

Cycle	20	40	60	80	100
I_{Si}	468798	468719	467512	467689	463654
I_{Ti}	17256	31798	42462	73141	100518
$R(I_{Ti}/I_{Si})$	0.0368	0.0678	0.0908	0.1564	0.2168
TEM-IP (nm)	1.24	2.01	2.88	4.64	6.38
T_{MEIS}^c (nm)	1.06	1.95	2.60	4.48	6.22
T_{TEM}^c (nm)	1.07	1.84	2.72	4.47	6.21
TEM-AC (nm)	1.60	2.56	3.20	4.80	6.71
T_{MEIS}^c (nm)	1.02	1.88	2.52	4.34	6.02
T_{TEM}^c (nm)	0.98	1.94	2.58	4.18	6.09

Figure 6. Linear plot between the thicknesses by TEM and MEIS intensity ratios of the TiO₂/Si (100) films.

the slope m and the offset value c were determined to be 28.7 and 0.169 nm, respectively. The calibrated thicknesses by MEIS (T_{MEIS}^c) and TEM (T_{TEM}^c) can be determined by the mutual calibration method from the equations $T_{MEIS}^c = R_{MEIS} \times 28.7$ and $T_{TEM}^c = T_{TEM} - 0.169$.

TEM thicknesses determined by the IP method show a much smaller offset value than that determined by the AC method. The linear plot between the TEM thicknesses by the AC method and the MEIS intensity ratios results in a slope m and an offset value c of 27.75 and 0.62 nm, respectively. The difference in the slope values of the two methods was small to be 3.3 %. However, the difference in the offset values between the IP method (0.17 nm) and AC method (0.62 nm) is large, being up to 0.45 nm. This reveals that the TEM thickness determined by the IP method is much closer to the real values than those by the AC method.

3.2. Thickness measurement by MCM with TEM and XPS

The thickness of the TiO₂/Si (100) films was also measured by mutual calibration with XPS and TEM, as shown in Table II. Figure 7 shows the linear fitting results for the thicknesses by XPS and TEM determined by the IP method. The results of the linear fit show a slope value of 1.053 and an offset value of -0.275 nm, respectively. The calibrated thickness by XPS (T_{XPS}^c) and TEM (T_{TEM}^c) can be determined by the mutual calibration method from the equations $T_{XPS}^c = T_{XPS} \times 1.053$ and $T_{TEM}^c = T_{TEM} + 0.275$.

The calibrated thicknesses by XPS are much thicker than those by MEIS in the range between 0.34 to 0.62 nm, which corresponds to a difference range from 5.3 to 26.4 %. This large difference is related with the difference in the offset values of XPS and MEIS. The linear

Table II. Thicknesses of the TiO₂/Si (100) films measured by XPS and TEM with IP method.

Cycle	20	40	60	80	100
TEM (nm)	1.24	2.01	2.88	4.64	6.38
XPS (nm)	1.37	2.17	3.06	4.74	6.24
T_{TEM}^c (nm)	1.52	2.29	3.16	4.92	6.66
T_{XPS}^c (nm)	1.44	2.29	3.23	4.99	6.57

Figure 7. Linear plot of the thicknesses of the TiO₂/Si (100) films measured by TEM and XPS.

Figure 8. Linear plot of the thicknesses of the TiO_2/Si (100) films measured by MEIS and XPS calibrated by TEM thicknesses determined by IP method.

fitting of the thicknesses by XPS and MEIS calibrated by TEM thicknesses determined by the IP method shows a large offset mismatch of 0.45 nm, as shown in Fig. 8. The thickness by MEIS is correctly proportional to the number of the constituent atoms in the film material. However, the peak intensities of XPS sensitively depend on the experimental parameters. For the precise thickness measurement by XPS from the equation $T_{\text{TiO}_2} = L \cos \theta \ln(R_{\text{exp}}/R_0 + 1)$, the detailed experimental parameters such as the $R_0 (= I_{\text{TiO}_2}^{\infty}/I_{\text{Si}}^{\infty})$ value, $R_{\text{exp}} (= I_{\text{film}}^{\text{exp}}/I_{\text{sub}}^{\text{exp}})$ value, and electron emission angle should be accurately determined. In particular, in the case of a large kinetic energy difference between the photoelectrons from the film and the substrate, the surface contamination layer should be well removed, and the effect of the contamination should be adequately considered.

4. Conclusion

The thicknesses of ultra-thin TiO_2/Si (100) films grown by ALD were measured by HR-TEM, MEIS, and XPS. The absolute thicknesses of the TiO_2/Si (100) films could be determined by mutual calibration with a combination of HR-TEM and MEIS. In the thickness measurement by HR-TEM, the inflection point method was found to be better than the average contrast method for the determination of the locations of the interface and the surface. The thicknesses were also determined by mutual calibration with HR-TEM and XPS. The thicknesses by the two mutual calibration methods showed a large offset mismatch of 0.45 nm. The origin of this result is the incorrect R_0 value due to the surface contamination layer. Whereas MEIS is free from the influence of the surface contamination layer, XPS is very sensitive to the surface contamination layer. In conclusion, for the thickness measurement of TiO_2/Si (100) films by XPS, the surface contamination layer should be well eliminated, and the effect of the surface contamination layer should be adequately considered.

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