Extended Abstract of PSA-19

O-04

Issues on thickness measurements of nm HfO_2 film by X-ray photoelectron spectroscopy

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(Received: June 4, 2019; Accepted: July 17, 2019)

In the mutual calibration for determination of ultrathin oxide film thickness, the thickness measured by X-ray photoelectron spectroscopy (XPS) has been known to be representative offset traceable. The offset traceability of XPS has been proved in the Consultative Committee for Amount of Substance (CCQM) pilot study P-190. For the analysis of nm HfO_2 film thickness by XPS, a general equation is used involving the relative peak intensity (R_o) of pure HfO_2 film and the substrate. The difference in the surface polarity of HfO_2 film and substrate induces different amount of surface carbon contamination, which leads to the error in R_o value. In the plot of XPS and reference thickness of HfO_2 films, the correction for the carbon contamination results in the offset value of -0.014 nm, while a larger offset value of -0.219 nm was measured without the carbon correction. Furthermore, different from the thickness measurement of SiO_2 film, the reference geometry configuration is not important factor for the thickness measurement of ultrathin amorphous HfO_2 films.

1. Introduction

Manufacturing of ultrathin oxide films is of key importance in semiconductor industries. To ensure the manufacturing quality control of ultrathin gate oxide, the validation and traceability in the measurement of gate oxide films need to be established. Therefore, CCQM P-38[1] was performed to compare measurements of ultrathin SiO_2 films. In the pilot study, the offset value of the oxide thickness measured by XPS was found to be zero. Based on this result, a mutual calibration method as shown in Fig. 1 was designed to determine the absolute thickness of nm oxide films. [2] Due to high-k dielectric property of HfO_2, a traceable thickness measurement of ultrathin HfO_2 films is required for advanced semiconductor industries. For this purpose, the thickness measurement of nm HfO_2 films was investigated in the recent CCQM pilot study P-190[3]. The certified reference thicknesses of six HfO_2 films were determined by mutual calibration between the average thicknesses of XPS and X-ray reflectivity (XRR). Transmission electron microscopy (TEM) and XRR can be used as length-traceable methods.

In this study, we explored the effect of surface carbon contamination to determine the HfO_2 thickness by XPS. Furthermore, we also verified the effect of setting the crystal geometry (34° emission angle and 22.5° in between the [011] and [001] azimuth) which has been known as an important factor for the SiO_2 film thickness [4].

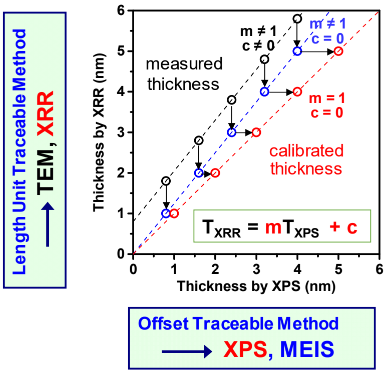

Fig. 1 Certification method of ultrathin oxide thickness by using mutual calibration

2. Determination of HfO_2 thickness by XPS

HfO_2(1~4 nm)/SiO_2(2 nm)/Si(100) films were grown onto Si (100) substrates by atomic layer deposition. The thickness of HfO_2 films (T_{HfO2}) can be determined by the following general equation (1) on the basis of the relative XPS peak intensity ratio (R_{exp}) of the HfO_2 ($I_{HfO_2}^{exp}$) and the substrate (I_{sub}^{exp}).

$$T_{HfO_2} = L\,cos\theta \ln\left(\frac{R_{exp}}{R_o} + 1\right) \qquad (1)$$

where L is the effective attenuation length (EAL) of photoelectrons ejected from HfO_2 film, θ is the photoelectron emission angle, and R_o ($=I_{HfO_2}^{\infty}/I_{sub}^{\infty}$) is the relative peak intensity of pure HfO_2 film ($I_{HfO_2}^{\infty}$) and substrate (I_{sub}^{∞}). The L was calculated by TPP-2M method and then calibrated by the mutual calibration plot of XPS and TEM thickness ($L = 1.939$ nm). Finally, the L was further calibrated by using the reference film thickness which was determined by the mutual calibration of XPS and XRR thicknesses reported in the pilot study P-190 ($L_{cal} = 1.826$ nm).

3. Effect of contaminated carbon correction

Thickness of contamination carbon, d_C, on thick HfO_2 and SiO_2 films was calculated using equation (2).

$$d_c = -L_{C1s} \cos\theta \ln\left(1 - \frac{I_{C1s}^{exp}}{I_{C1s}^{\infty}}\right) \qquad (2)$$

where L_{C1s} is the effective electron attenuation length for contaminated carbon, and I_{C1s}^{∞} is the XPS intensity of pure bulk contaminant. The average result for 14 organics reported previously[5] was used for the L_{C1s}. Fig. 2(a) shows the effect of isopropyl alcohol (IPA) soaking time on the carbon removal from pure HfO_2 and SiO_2 samples. The thickness of contaminated carbon layer on pure SiO_2 film decreases from 0.564 nm to 0.107 nm as increasing the soaking time. On the other hand, the carbon layer on pure HfO_2 film only reduced from 1.307 nm to 0.698 nm. After overnight soaking, the carbon layer for HfO_2 is 7 times thicker than that for SiO_2 sample, which causes error in the R_o value. The different desorption rate of contaminant carbon is attributed to the higher polarity of the Hf-O than the Si-O bond [6].

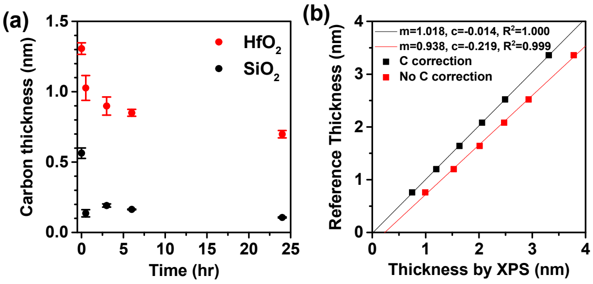

Fig. 2 (a) Carbon thickness change on reference HfO_2 and SiO_2 films depending on soaking time in isopropyl alcohol; (b) Effect of contaminated carbon correction on the HfO_2 thickness

In order to explore the effect of contaminated carbon on the HfO_2 thickness, the reference thickness was plotted as a function of the XPS thickness with and without the carbon correction as shown in Fig. 2(b). The carbon correction for the R_o value was performed by using equation (3).

$$I^{\infty} = I \exp\left(\frac{d_C}{L_{C1s} \cos\theta}\right) \qquad (3)$$

where I^{∞} is the reference peak intensity corrected for the carbon contamination and I is the measured intensity. With the carbon correction, we obtained an offset c value of -0.014, meaning that the XPS is offset traceable method. The larger offset value of -0.219 obtained without the correction is attributed by the error in the R_o value. The different contaminated carbon quantity on HfO_2 and substrate surfaces differently attenuates the Hf 4f and Si 2p reference peak intensity.

4. Effect of the crystal geometry configuration

In the previous study[4], the crystal geometry was an important factor to determine ultrathin SiO_2 thickness on Si(100). In order to verify the effect for HfO_2 film, we compared the thickness measured at 45° emission angle and at the reference geometry. As shown in Fig. 3, the slope and offset values are similar for both configurations. Therefore, the measurement geometry is not an important factor for the determination of HfO_2 film thickness because the reference substrate consists of about 2 nm thermal oxide layer.

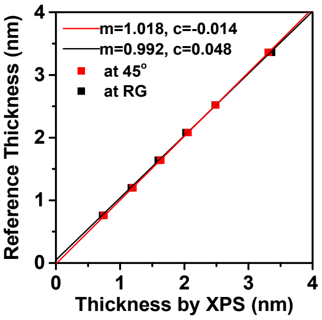

Fig. 3 Effect of reference geometry configuration on the HfO_2 thickness measured by XPS

4. Conclusion

We have explored the effect of both contaminated carbon correction and reference geometry configuration on determination of ultrathin HfO_2 thickness. The correction of contaminated carbon seriously affects the film thickness, which is associated with the different desorption rate of carbon contamination from the reference substrate and HfO_2 film. It leads to severe error in the R_o value and consequently a large offset value. The reference geometry configuration which is an important factor for the SiO_2 thickness measurement is not that critical to determine the HfO_2 thickness.

5. References

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