The study of the silicon oxide thickness on crystalline Si by X-ray photoelectron spectroscopy and spectroscopic ellipsometry

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The to study of the total oxide (SiO_2+SiO_x) thickness, SiO_2 and SiO_x (e.g. Si_2O, SiO, Si_2O_3) thicknesses on Si(100) crystalline substrate with take-off angles ranging from 30° to 80° has been carried out by spectrometric method. The d_s X-ray Photoelectron Spectroscopy (XPS) thicknesses were compared with d_{EL} thicknesses obtained by fitting the Spectroscopic Ellipsometry (SE) spectra. A qualitatively good correlation is revealed. However, from these estimations of film thicknesses it results that ellipsometry analysis cannot be as accurate as in XPS evaluation. This is due to uncertainty of used optical constants as well due to very thin oxide films used in this work.

1. Introduction

An XPS system is able to map out dielectric film physical thickness, chemical composition and the structure of layers for thin films. For practical applications where high-K gate dielectrics are required [1], it is essential to control the composition and transition layers at SiO_2/Si interface in Si oxidation processes [2,3]. In general, this thickness has been measured by ellipsometry and found to be quite reliable for thick oxide films.

However, when the oxide layer is thinner than about 10 nm, the ellipsometric thickness is not always reliable. Also, it is well known that large discrepancies exist for the photoelectron effective attenuation length (EAL) in SiO_2, where values from 2 to 4 nm have been reported [4÷7] and compared to theoretical predictions for inelastic mean-free path.

This critical parameter must be resolved so that XPS can become a standard method in thin-film thickness measurement. The EAL differs from corresponding inelastic mean free path (IMFP) on account of elastic scattering of signal photoelectrons.

In the present work Angle-resolved X-ray Photoelectron Spectroscopy (ARXPS) was performed on Si(100) surfaces with different types of oxides: native and thermally grown.

The analysis and computation of Si oxides film thickness were done ex-situ by Spectroscopic Ellipsometry (SE).

This paper compares the possibilities of ARXPS technique in the thickness measurement of SiO_2 layers thermally grown on single-crystalline surfaces with the performance of SE technique.

2. Experimental

The Si oxides were studied in both native and thermally grown (500°C from 0.5 to 5 hours) on Si substrate after a gentle state sputtering in 2 keV, 7.5 μA Ar^+ plasma (5 minutes) to remove adsorbed oxygen and organic species.

The VG Scientific ESCA3 MK II spectrometer with an anti-cathode of Mg ($E_{k\alpha}$=1253.64 eV) at 300 W was used to study the SiO_2/Si interface. In this view the XPS equipment was operated in the constant energy mode with a pass energy of 10 eV on 256 channels, 200 ms dwell time/channel, 10 scanning/spectrum and 20 eV analyzer resolution. The analysis chamber is maintained at ultra high vacuum (~10^{-9} torr). For ARXPS analysis the take-off angle (TOA) was defined according to ASTM E 673-03 document, Standard Terminology Relating to Surface Analyses, as the angle θ at which the photoelectrons leave a probe relative to the plane of the probe surface (Fig.1).
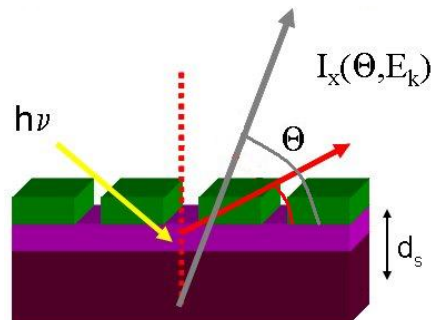

Fig.1. Effective information depth d_s varies with polar angle θ or take off-angle (TOA).

The total oxide (SiO$_2$+SiO$_x$) thicknesses, SiO$_2$ and SiO$_x$ (e.g. Si$_2$O, SiO, Si$_2$O$_3$) thicknesses on Si(100) crystalline substrate were studied with TOA's: 30°, 40°, 50°, 55°, 60°, 70°, 80°. The XPS recorded spectra are processed using SDP v 2.3 and S-PROBE software.

The SDP software can be used to measure the peak area and the background, to fit the background with a linear baseline, to record the intensity, the full-width at half-maximum (FWHM) and the endpoints of peaks.

The same background shape and endpoints are used whenever the acquisition of spectrum is repeated. The Si2p line with BE=99.6 eV [7, 8] was the reference to determine the charging potential of Si probe surface by comparing with the experimentally determined binding energy (BE) of XPS lines. The nominal value of 285.0 eV for C1s line of adventitious carbon often used for the BE's of the relevant peaks is not considered as reference for the particular case of the present work, because for SiO$_2$/Si samples it is found that the C peak position tends to change relative to the Si (substrate) peak position [9]. In a previous work [10] using C1s line of adventitious carbon as reference was obtained an offset of 0.1 eV in the position of Si2p line.

The ellipsometry measures the spectra of two angles (Ψ, Δ) as function of photon energy E(eV) or light wavelength λ(nm). Tan (Ψ) represents the ratio of the two amplitudes of the electric field components (perpendicular on the plane of incidence and parallel to the plane of incidence, respectively), while Δ is the phase difference between the mentioned two waves.

The complex reflection coefficient is defined as [11]:

$$\rho = \frac{\widetilde{R}_p}{\widetilde{R}_s} = \tan(\Psi)e^{j\Delta} = \frac{E_{rp}/E_{ip}}{E_{rs}/E_{is}} \qquad (1)$$

where $\widetilde{R}_p$ and $\widetilde{R}_s$ are the Fresnel coefficients corresponding to the two mentioned polarization states, parallel (p) and perpendicular (s), respectively.

The interpretation of the as measured data is difficult and therefore an optical model is required in order to obtain the physical parameters of the sample such as refractive index n, extinction coefficient k and thickness.

Optical measurements are done ex-situ with a Woollam Variable Angle Spectroscopic Ellipsometer (VASE) system, equipped with a high pressure Xe discharge lamp incorporated in an HS- 190 monochromator. Measurements are performed in the visible and near-UV region of the spectrum at wavelengths between 190 and 900 nm, step of 10 nm, at 50°, 52.5°, 55°, 57.5°, 60° angle of incidence.

Bulk dielectric functions of the layers are taken from literature [12].

In the present work we make use of WVASE32 software, which is designed to handle data modeling and fitting from simple single film problems to extremely complex multisample and multi-layers problems.

3. Results and discussion

The oxide thickness is determined by the Si2p core level intensity ratio of the oxidized silicon film I_{ox} and substrate silicon I_{Si} by:

$$d_x = \lambda_{Si} \sin\theta \ln\left(\frac{1}{0.84}\frac{I_{ox}}{I_{Si}}+1\right)(\text{Å}) \qquad (2)$$

from [7], where θ is TOA and λ_{Si} is escape depth of the photo-electrons from Si substrate in SiO$_2$ overlayer for photon energy of hυ=200 eV. XPS becomes a linear method for being repeatedly possible, if the reference geometry (the polar and azimuthal angles) and the count numbers of the Si2p peaks are accurately controlled. Since the Si oxide and Si bulk 2p peaks are well separated, I_{ox} and I_{Si} can be easily determined by integrating the peak area after a linear background substraction. The escape depth of Si2p photoelectrons from SiO$_2$ matrix has been reported in a wide range from 2 to 4 nm and predicted from the theoretical inelastic mean free path. In this work the computation of oxides film thickness on crystalline Si is done with escape depth λ_{Si}=27 Å. This value was experimentally determined by Yano et al. (1994) [7] using the XPS results and cross-sectional transmission electron microscope (TEM) observations of a several nanometer thick thermal Si oxide on Si. In reference [13] a TEM micrograph and an XPS Si2p core level spectrum show an amorphous SiO$_2$ film on Si(100) crystalline substrate but don't highlight the structure of Si/SiO$_2$ interface. It is mentioned that one atomic layer variation is certainly possible due to the intrinsic two domain interface structure with each domain differing by one atomic step height. A three layers models (Si/SiO$_x$/SiO$_2$) is prerequisite for a complete characterization of such samples, because the depth distribution is of high importance for the understanding of the process of thermal decomposition of SiO$_x$ layer [14].

Fig. 2 shows a high resolution Si2p XPS spectrum for TOA=30° recorded from a native oxidized sample.
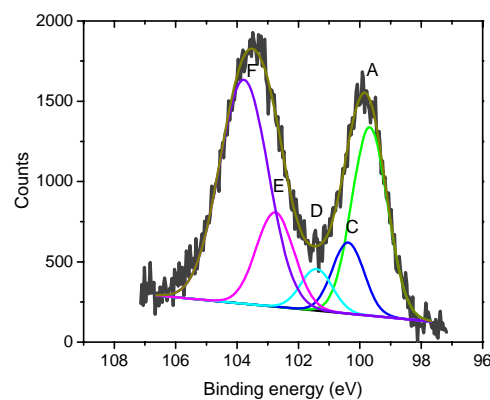

Fig.2. XPS spectrum in the Si2p region at TOA=30° for SiO$_2$ native oxidized surface: (A)-Si2p line: 99.6 eV, (C)-Si$_2$O line: 100.43 eV, (D)-SiO line: 101.58 eV,

(E)-Si$_2$O$_3$:102.96 eV, (F)-SiO$_2$:103.72 eV

Although, the decomposition has a slight arbitrary degree. In TOA=30° spectrum the Si$_2$O (intermediate oxide) peak (C) enters under bulk Si peak much more than in TOA=80° spectrum (Fig. 3).
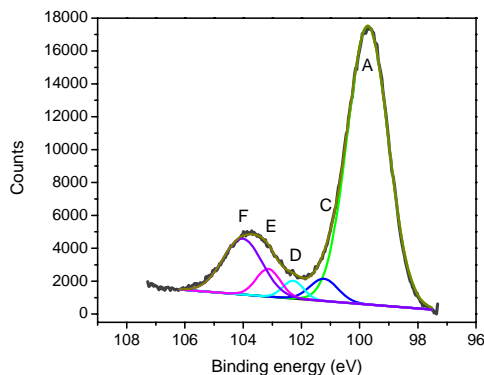

Fig.3. XPS spectrum in the Si2p region at TOA=80° for SiO$_2$ native oxidized surface: (A)-Si2p line: 99.6 eV, (C)-Si$_2$O line: 100.67 eV, (D)-SiO line: 101.76 eV, (E)-Si$_2$O$_3$:103.02 eV, (F)-SiO$_2$:103.92 eV

The 2p spin-orbit splitting, p$_{3/2}$ and p$_{1/2}$, is not resolved for bulk silicon substrate (X-ray source is not monochromatic) and for the oxide film due to the amorphous nature of SiO$_2$ structure.

The interface contains probably few atomic layers of Si atoms in intermediate oxidation states i.e. Si^{1+}(Si$_2$O), Si^{2+}(SiO) and Si^{3+}(Si$_2$O$_3$). A second region extends about 30 Å into SiO$_2$ overlayer [6], where the SiO$_2$ is compressed because the density of Si atoms is higher for Si substrate than for SiO$_2$ overlayer.

On the other hand Figs. 2, 3 show a slight increasing in the offset between the SiO$_2$-Si$_2$O$_3$ convolutions and the Si-Si$_2$O convolutions with the increasing in TOA.
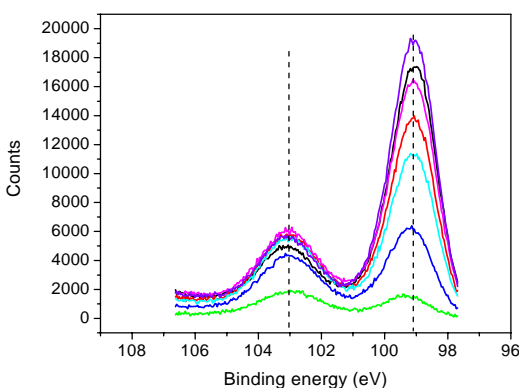

Fig. 4. Superposed ARXPS proportional spectra from SiO$_2$ native oxidized surface for Si2p and SiO$_2$2p lines (TOA=30°, 40°, 50°, 55°, 60°, 70°, 80°). TOA increases from 30°-bottom spectrum to 80°-upside spectrum.

The both facts are possible because the distribution of charging in oxides overlayer varies with the depth (more charging for thicker SiO$_2$). It is already known that SiO$_2$ films as thin as 3 nm can be used as a MOS gate oxide [15]. It has been known for a long time that under X-ray irradiation, charges can accumulate at the SiO$_2$/Si interface [16]. It is also known that SiO$_2$ can withstand electric fields of 10^6-10^7 V/cm [17]. This means that a voltage difference of 0.3-3 V can be induced in a 3 nm-thick SiO$_2$ film if enough charges are introduced into the SiO$_2$. In view of these considerations, it is surprising that so few investigators report charging in these thin SiO$_2$ films during XPS measurements. One exception is Grunthaner et al. [18] who found that there was indeed charging but claimed that these charges can be neutralized by electron irradiation as we have proceeded (0.2 mA, 1 eV). In all probability, complete neutralization was not accomplished because the sample (SiO$_2$/Si) was inhomogeneous and the energy distribution of the irradiated electrons is not the same as that of the emitted photoelectrons. Electron irradiation is normally used to *control charging* rather than for complete neutralization. The sample is not homogeneous, so that charges can accumulate not only near the SiO$_2$ surface but also near the SiO$_2$/Si interface. This means that charges of opposite sign accumulate on the Si side of the interface. The neutralizing effect of electrons is greater at the surface than in the SiO$_2$ or Si. There is no guarantee that electron irradiation which neutralizes the surface charges can equally neutralize the interface charges and vice versa. If some of the surfaces positive charges (near the SiO$_2$ surface) remain un-neutralized, they are thought to be compensated for by an equal amount of negative charges, or to be more exact, an electric double layer is formed at the SiO$_2$ surface.

If this is not a double layer, the measured chemical shift is expected to change for thicker SiO$_2$ films.

However, the chemical shift is found to be roughly constant for thicknesses above about 3 nm, as it can be inferred from Fig. 6. This means that the positive oxide charges discussed before at the SiO$_2$ side of SiO$_2$/Si interface are not compensated for by these electrons on the SiO$_2$ surface. On the other hand, negative charges can easily be supplied on the Si side of the interface from the ground.

For TOA=30° the detected photoelectrons escape from a layer near of surface, they roam across a thinner layer of oxides than for TOA=80°.

The increasing in BE of the Si2p line (without charge compensation) for TOA==80° corresponds to a decreasing in kinetic energy with the depth for the photoelectrons that arrive from substrate.

This relative decreasing in kinetic energy can be correlated with the distribution of fixed charges inherently present in overlayer, more charging to substrate than near of surface.

But, for the same TOA a significant shift can be produced by electric charging in these oxide films due to X-ray irradiation in successive measurements [16], thus contributing to the oxide thickness dependence of the chemical shift.

This shift is not due to changes in the chemical state of the oxides film because the O1s peak also shifts in the same direction as the Si2p (oxide) peak and by the same amount [9]. The O1s/Si2p (oxide) BE ratio is not changed by X-ray irradiation. If chemical state changes, the Si2p and O1s peaks would have shifted in opposite directions.

It is not easy to correct for this charging. One way is to neutralize it by electron irradiation, but it is not sufficient merely to adjust the surface potential, since the emitted photoelectrons have various kinetic energies (escape depths) and making the SiO_2 potential the same as that of the spectrometer does not in general enssure that the potential is also the same at the SiO_2/Si interface (on the Si side).

The optical model used for SE consists of 3 layers: the Si substrate, the SiO_x interface and the SiO_2 layer. This model for SE evaluation of oxides thicknesses is the same as that one described by Herzinger et al. [12].

SE can measure thickness differences of 0.2 nm between two different SiO_2 layers, but it is questionable in determining extremely low thicknesses (below 3nm), without have the optical constants with certainty determined.

Considering a single interface the Fresnel coefficients are defined as:

$$r_p \equiv \frac{E_{rp}}{E_{ip}} = \frac{\tilde{n}_t \cos(\theta_i) - \tilde{n}_i \cos(\theta_t)}{\tilde{n}_t \cos(\theta_i) + \tilde{n}_i \cos(\theta_t)} \tag{3}$$

$$r_s \equiv \frac{E_{rs}}{E_{is}} = \frac{\tilde{n}_i \cos(\theta_i) - \tilde{n}_t \cos(\theta_t)}{\tilde{n}_i \cos(\theta_i) + \tilde{n}_t \cos(\theta_t)} \tag{4}$$

as function of the refractive indices of incident and transmitted medium and of the incidence and refraction angle. In the case of a single thin film each Fresnel coefficient is expressed as function of reflection coefficients of each interface by:

$$r_{012} = \frac{r_{01} + r_{12}e^{-i2\beta}}{1 + r_{01}r_{12}e^{-i2\beta}} \tag{5}$$

where indices 0, 1, and 2 corresponds to ambient, thin film and substrate, respectively. β is the phase difference and is given by:

$$\beta = \frac{2\pi d}{\lambda}\tilde{n}_1 \cos(\theta_1) \tag{6}$$

where d is the thin film thickness and λ is the wavelength. Considering as unknown fit parameters in a thin film optical model the film thickness and the refractive index, and performing the fit routine in zone where $\tilde{n}_1$ is a real number (the extinction coefficient k = 0), it will end up with a unique solution (n, d) which satisfies the (Ψ, Δ) experimental values. This holds only when d has reasonable values (>3nm). For smaller thickness values the (n, d) pair can not be anymore extracted exactly, and the

only sensitive physical parameter is the optical thickness n*d. In the case of our optical model the reflection coefficients can be derived by using the original Abeles matrix algorithm [19, 20, 21]. Each reflection coefficient is expressed by [11]:

$$r_{012} = \frac{r_{01} + r_{12}e^{-i2\beta_1} + (r_{01}r_{12} + e^{-i2\beta_1})r_{23}e^{-i2\beta_2}}{1 + r_{01}r_{12}e^{-i2\beta} + (r_{12} + r_{01}e^{-i2\beta_1})r_{23}e^{-i2\beta_2}} \tag{7}$$

The number of unknown parameters will be 4 (if both k=0) or 6. In the work done by Herzinger et al. [12] on thicker thin SiO_2 films are described different approaches to extract the true parameters by ellipsometry. In this work we input their dielectric functions of Si, SiO_x and SiO_2. Since the dielectric function of SiO_x interface, depends on its stoichiometry and inter-atomic distances [22], and because the present work lies at the detection limit of ellipsometry, an extended model will not improve considerably the metrology of such samples. In Figure 5 are presented the ellipsometry spectra acquired on a bare silicon substrate and on a sample thermally treated at 500°C for 1.5h.
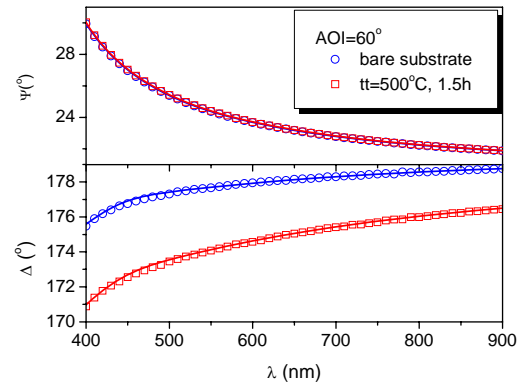

Fig. 5. SE spectra of the bare substrate (circles) and the sample thermally treated for 1.5h (squares). The solid lines are obtained form the fitting procedure described in the text.

The Ψ spectra are almost identical. These indivisible spectra are similar to those obtained by conventional spectroscopy (reflectivity measurements). The unique feature of ellipsometry, represented by Δ values, shows a clear difference of several degrees between the two samples.

The lines from Fig. 5 represent the generated data by using the described model after the fitting procedure.

By the SE method can be also estimated the thicknesses of the two layers: SiO_x and SiO_2.

In the case of the bare sample the results are d_{EL} SiO_x= 8±0.6 Å and d_{EL} SiO_2= 7±0.8 Å, whereas for the thermally treated sample the thicknesses are d_{EL} SiO_x= 5.3±1 Å and d_{EL} SiO_2= 37.5±1.2 Å.

The results shown in Fig. 6, where the XPS thickness results d_s were compared with d_{EL} thickness obtained from Spectroscopic Ellipsometry (SE) measurements,

concluded that the ARXPS analysis was the most sensitive for oxide thicknesses from 1.5 to 3 nm.
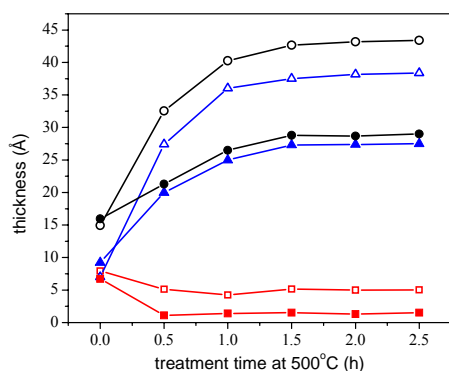

Fig. 6. XPS (d_s) and SE (d_{EL}) thickness results for Si oxides measurements versus thermal treatment time (■SiO_x (d_s), □SiO_x (d_{EL}), ▲SiO_2 (d_s), ●SiO_2+SiO_2(d_s), △SiO_2 (d_{EL}), ○SiO_x + SiO_2 (d_{EL})) at constant 500 °C temperature.

The curves for the estimated oxide thicknesses versus thermal treatment time have the same configuration both for XPS determination and for ellipsometric analysis. A good correlation is obtained as long as d_s and d_{EL} are measured after thermal oxidation of 0.5÷2.5 hours.

As the treatment time increases, SiO_x, SiO_2 and also SiO_x+SiO_2 thicknesses reach a plateau. The higher thickness of SiO_2 layer limits the oxidation process of Si underneath and after high temperature annealing appears a redistribution of Si and O atoms incorporated at interface. From the both experimental methods, a decrease of interfacial SiO_x layer is revealed. There is a competition of two processes: one, the formation of Si inclusions in the SiO_2 matrix and two, the diffusion of Si atoms in the direction of the surface of the Si/SiO_2 layer [14].

The results d_{EL} for SE measurements (ex-situ) are larger than d_s from XPS measurements (in-situ) after entrance in plateau or saturation range of oxides layers for thermal treatment time greater than 1 hour. The differences in measured thicknesses accounted to 4 Å for SiO_x, 10 Å for SiO_2 and thus to 14÷15 Å for SiO_x+SiO_2 layer thickness. Also, the difference between SiO_2(d_s) and SiO_2(d_{EL}) is predominant in the difference of the total SiO_x+SiO_2 thickness.

The SiO_2 thickness of 3 nm is an average value between measured SiO_2(d_s) and SiO_2(d_{EL}) thicknesses and it is an important threshold in the sensitivity of thickness measurements by XPS and SE methods [7].

The measured SiO_x(d_s) and SiO_x(d_{EL}) thicknesses are situated at the down limit of measurement possibilities for XPS technique, respectively for SE method.

There is a difference in measurement possibilities of XPS and SE for amount of SiO_x at SiO_2/Si interface estimated to be between a little less than one Si monolayer (for native oxide) and respectively a few Si monolayers (for thermal grown oxides). Errors of a few tenths of a nm

are of no importance when we have oxide films thicker than 100 nm, but it is a serious problem for oxide films with thickness of 2.5÷4 nm as in the bottom case in Fig. 6.

However, d_{EL} is found to increase gradually if the sample is left in air and it is larger by several tenths of a nm after a month in air at about 50% relative humidity and at room temperature [9]. This difference in Fig. 6. The difference increases with the amount of hydrocarbons adsorption on the sample surface. The hydrocarbons are known to adsorb onto SiO_2 and the amount adsorbed increases with the time of storage in air, which might influences d_{EL}. On the other hand, the XPS thickness d_s is independent of adsorption because it is obtained from the intensity of Si2p (oxide) photoelectrons. To be more exact, the effect of adsorption is the same for the Si2p (oxide) and Si2p (substrate) photoelectron intensities.

However, from these initial estimations of film thicknesses it results that ellipsometry method cannot be as accurate as XPS in the evaluation of thinner films.

This is due to uncertainty of used optical constants as well due to very low thicknesses used in this work.

4. Conclusions

The ellipsometry technique can measure thickness differences of 0.2 nm between two different SiO_2 layers. The thickness d_s is consistent in case of thermal treatment time at 500°C with the measured chemical shift (including charging) and the ellipsometry thickness d_{EL}. The results d_{EL} for SE measurements are larger than d_s from XPS measurements by 4÷15 Å.

A good correlation of the curve profiles of is obtained within the accuracy of our measurements as long as d_{EL} is measured after 0.5÷2.5 hours of thermal oxidation.

The difference between XPS results and SE results is very small (1÷3 Å) when the samples are left in air (native oxides). This difference increases after the thermal treatment.

The XPS measurement was most sensitive to differences on films < 3 nm thick.

On the other hand, the effects of electrical charging on chemical shifts or peak positions in XPS must be corrected in order to obtain conclusions consistent with as much experimental data as possible regarding the SiO_2/Si structure.

For practical purpose it is possible to use XPS for accurate thickness evaluation of oxide films less than about 10 nm. This can be done if it is possible to define the oxide (SiO_2) peak shape in the Si2p spectra and if the value of the Si2p photoelectron effective attenuation length or escape depth is known. The obtained thickness value can be calibrated by some standard such as the ellipsometric thickness.

The ellipsometric thickness must be measured carefully so that the effect of the adsorption layer becomes the same and/or small for all thicknesses. A one-to-one relation between d_s and the ellipsometric thickness d_{EL} can be found if d_{EL} is carefully measured right after oxidation.

The zero point of the thickness can be set by defining such an oxide peak whose intensity becomes zero for a freshly chemical etched Si sample or other standard state. It is easier to define the oxide peaks for a high-resolution Si2p spectrum if the intermediate oxide peaks clearly separated from the Si substrate peak like for TOA=30° spectrum. In this case the intensities of the small peaks between SiO$_2$2p and Si2p lines correspond to a thickness less than 0.1 nm. Thus, by using only SiO$_2$ and Si substrate peaks, therefore requiring no questionable peak decomposition, it is possible to obtain the oxide thickness with accuracy much better than ±0.1 nm.

On the other hand, errors due to oxide defects may arise for XPS oxide thicknesses greater than ~ 10 nm. The correlation ellipsometric-XPS measurements sometimes breaks down at thicknesses above ~ 10 nm. In these cases, it is found that d_s is considerably smaller than d_{EL}. This is probably due to defects (pinholes, Si clusters or thickness nonuniformity) in the SiO$_2$. For obtaining the XPS thickness d_s, it was assumed that the oxide films are uniform. When this assumption breaks down, the correct thickness by XPS cannot be obtained.

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