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Surface chemical analysis — X-ray photoelectron spectroscopy — Measurement of silicon oxide thickness

Analyse chimique des surfaces — Spectroscopie de photoélectrons par rayons X — Mesurage de l'épaisseur d'oxyde de silicium

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ISO 14701 was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 7, *X-ray photoelectron spectroscopy*.

Introduction

The measurement of the thickness of silicon oxide at the surface of silicon wafers has been conducted in the past by many methods. These generally apply to oxide layers thicker than 20 nm. It is often important to measure thicknesses in the range below 10 nm, and this International Standard addresses the range below 8 nm using X-ray photoelectron spectroscopy. Problems arise in measuring film thicknesses in this thickness range since, for a layer to bond well to the substrate, it must form strong inter-atomic bonds at the interface so that a monolayer or more of layer and substrate interfacial material exists there. This material would not necessarily be a thermodynamically stable bulk material. Additionally, if the layer is reactive, its outer surface might have reacted with the environment and so be changed between fabrication and measurement. For the particular case of silicon dioxide on silicon, at the interface there is approximately a monolayer of sub-oxides and, at the surface, adsorbed materials containing carbon, oxygen and probably hydrogen atoms. These effects lead to offsets for the thicknesses deduced from many methods that, whilst reliably measuring changes in thickness between one specimen and another, have difficulty in defining an absolute thickness.

The procedures described in this International Standard provide methods to measure the thickness with high accuracy (optimally 1 %) and also, more rapidly and simply, at lower accuracy (optimally 2 %). It could also form a basis for the measurement of many film thicknesses on substrates, but, without considerable further work, the uncertainties will be undefined.

Surface chemical analysis — X-ray photoelectron spectroscopy — Measurement of silicon oxide thickness

1 Scope

This International Standard specifies several methods for measuring the oxide thickness at the surfaces of (100) and (111) silicon wafers as an equivalent thickness of silicon dioxide when measured using X-ray photoelectron spectroscopy. It is only applicable to flat, polished specimens and for instruments that incorporate an Al or Mg X-ray source, a specimen stage that permits defined photoelectron emission angles and a spectrometer with an input lens that can be restricted to less than a 6° cone semi-angle. For thermal oxides in the range 1 nm to 8 nm thickness, using the best method described in this International Standard, uncertainties, at a 95 % confidence level, could typically be around 2 % and around 1 % at optimum. A simpler method is also given with slightly poorer, but often adequate, uncertainties.

2 Symbols and abbreviations

2.1 Abbreviations

HPLC   high-purity liquid chromatography

IPA   isopropyl alcohol

2.2 Symbols

The term intensity is used below and elsewhere. This refers to a measurement of peak area in the spectrum after relevant background subtraction.

d_{oxide} total oxide thickness

d_{Si_2O} thickness contribution to the Si_2O peak

d_{SiO} thickness contribution to the SiO peak

$d_{Si_2O_3}$ thickness contribution to the Si_2O_3 peak

d_{SiO_2} thickness contribution to the SiO_2 peak

I_{Si} intensity of the Si contribution to the Si 2p peak

I_{Si_2O} intensity of the Si_2O contribution to the Si 2p peak

I_{SiO} intensity of the SiO contribution to the Si 2p peak

$I_{Si_2O_3}$ intensity of the Si_2O_3 contribution to the Si 2p peak

I_{SiO_2} intensity of the SiO_2 contribution to the Si 2p peak

L_{Si} attenuation length for Si 2p electrons in Si

$L_{\mathrm{Si_2O}}$	attenuation length for Si 2p electrons in $\mathrm{Si_2O}$
L_{SiO}	attenuation length for Si 2p electrons in SiO
$L_{\mathrm{Si_2O_3}}$	attenuation length for Si 2p electrons in $\mathrm{Si_2O_3}$
$L_{\mathrm{SiO_2}}$	attenuation length for Si 2p electrons in $\mathrm{SiO_2}$
$R_{\mathrm{Si_2O}}$	intensity normalization parameter for the $\mathrm{Si_2O}$ contribution to the Si 2p peak
R_{SiO}	intensity normalization parameter for the SiO contribution to the Si 2p peak
$R_{\mathrm{Si_2O_3}}$	intensity normalization parameter for the $\mathrm{Si_2O_3}$ contribution to the Si 2p peak
$R_{\mathrm{SiO_2}}$	intensity normalization parameter for the $\mathrm{SiO_2}$ contribution to the Si 2p peak
U_{n}	uncertainty contribution, at a 95 % confidence level, for the spectrum measurement statistics
U_{θ}	uncertainty contribution, at a 95 % confidence level, for θ
U_{A}	uncertainty contribution, at a 95 % confidence level, for the analyser electron optics defining the solid angle of acceptance
U_{E}	uncertainty contribution, at a 95 % confidence level, for the validity of the equations for thicknesses
U_{F}	uncertainty contribution, at a 95 % confidence level, for peak synthesis without the intermediate oxides
U_{L}	uncertainty contribution, at a 95 % confidence level, for the attenuation length
θ	angle of emission of electrons measured from the surface normal

3   Outline of method

Here, the method is outlined so that the detailed procedure, given in Clause 4, can be understood in context. Typical spectra are available in the literature and given later in Figures 3 and 4.

The initial step of cleaning the specimens, if necessary, is given in 4.1. In 4.2 and 4.3, the specimens are mounted and suitable spectrometer settings chosen. In 4.4 and 4.5, the procedures for recording the data and measuring the intensities are given. Finally, in 4.6 and 4.7, the oxide thickness and its uncertainty at a confidence level of 95 % are calculated. In 4.5 and 4.6, two methods are provided for calculating the oxide thicknesses from the data: a more complex method with better uncertainties and a simpler method with poorer uncertainties. The more complex method might achieve uncertainties as low as 1 %, but the simpler method is restricted to uncertainties that are greater than 2 %. This greater figure is often adequate for many purposes, however. The sequence of steps is illustrated in the flowchart in Figure 1. It might be useful to refer to this during use of this International Standard.
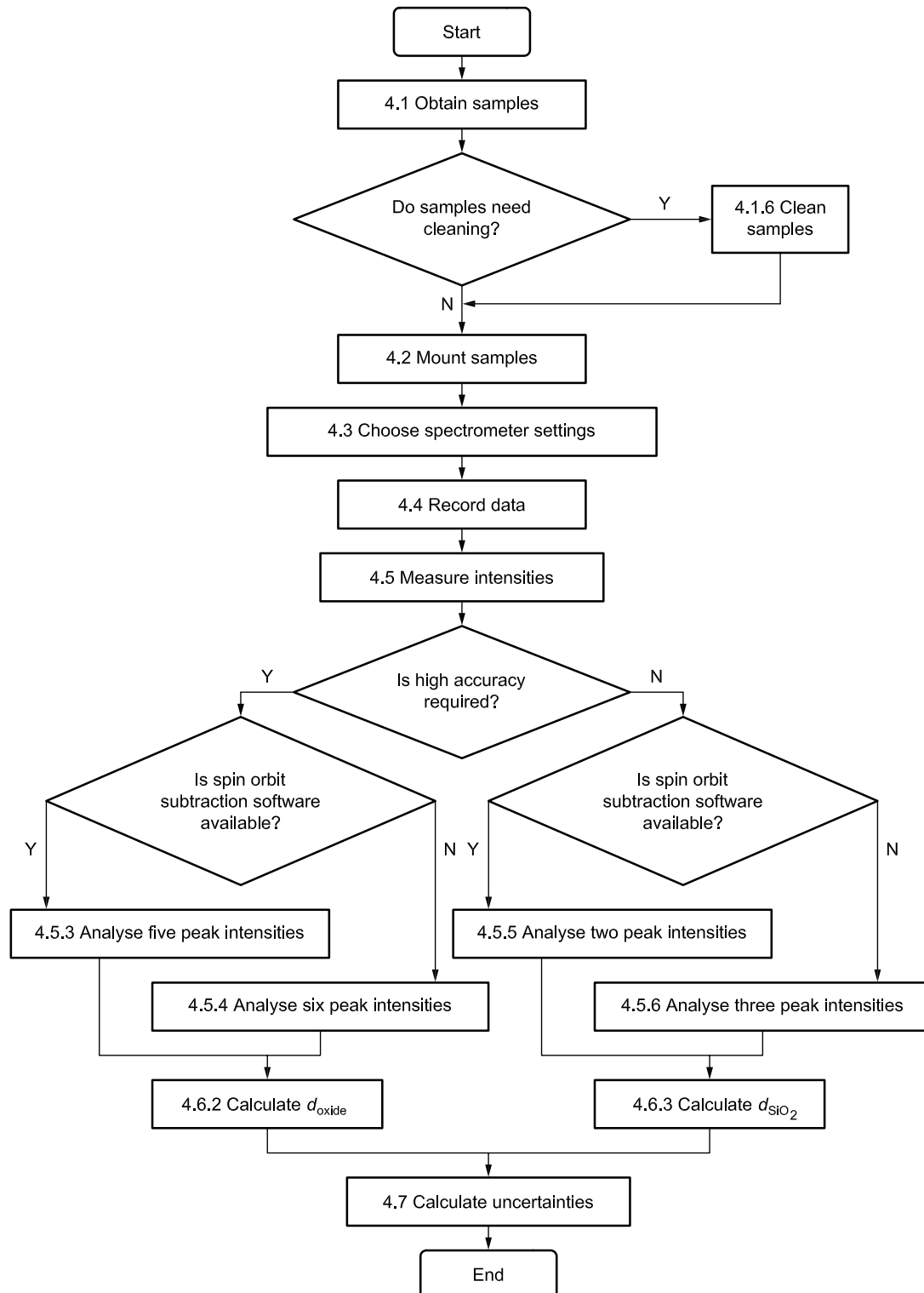
Figure 1 — Flowchart of the measurement process
(Y and N at decision points are the usual "yes" and "no", respectively)

Subclause 4.3 requires the angle of emission to be set accurately, and it is often the accuracy of this setting that limits the final accuracy. Users of this procedure will have to ensure that the accuracies of these settings are known in order to evaluate the final uncertainty. The settings can be checked to an adequate level using reflectors mounted on the specimen stage, a laser beam and standard geometrical relationships[1][2].

4 Method for measuring the oxide thickness

4.1 Cleaning and preparing the specimen

4.1.1   For cleaning and preparing the specimens, gloves and uncoated stainless-steel tweezers are required. In selecting gloves, care shall be taken to avoid those with talc, silicone compounds or similar contaminants. "Powder-free" gloves have no talc, and fresh polyethylene gloves, or gloves of a higher quality, shall be used in specimen handling. Do not use moulded gloves, for example vinyl, which will probably be covered with highly contaminating release agents. Tweezers that are of uncoated stainless steel shall be used.

4.1.2   To manipulate specimens, the gloves are used to hold the tweezers and not the specimen. Avoid any wiping materials, sometimes used to handle specimens, as they might result in unwanted contamination of the specimen surface. Unnecessary contact of the specimen with the gloves shall be avoided. Specimen mounts and other materials used to hold specimens shall be cleaned regularly whenever there is a possibility of cross-contamination of specimens. The use of tapes containing silicones and other mobile species shall be avoided.[3]

4.1.3   Specimens shall be prepared and mounted with clean tweezers to ensure that the surface is not altered prior to analysis and that the best possible vacuum conditions are maintained in the analytical chamber. Use the gloves to handle the tweezers to avoid contaminating them or any cleaning equipment with finger grease. Clean the tweezers by one of the following two methods:

a)   Immerse the tweezers before use for 16 h in high-purity liquid chromatography (HPLC), or equivalent, grade (>99,5 %) isopropyl alcohol (IPA) that leaves no significant residue. Next, remove the liquid, renew the IPA, agitate ultrasonically for 1 min, rinse in fresh IPA and remove the excess liquid using a jet of pure, dry argon or another inert gas.

b)   Boil the tweezers in ultra-high-purity water for 10 min.

Grip the specimen at the edge only, in a region that will not be analysed. Avoid breathing or speaking over the specimen. Keep these tweezers in a clean, glass container for future use. Tools shall not unnecessarily touch the specimen surface to be analysed.

4.1.4   Inspect the specimens for any scratches, blemishes or marks on the polished surfaces. Finger marks should not be present but, if they are, may be removed as described in 4.1.6. Note the condition of the surface. It should be featureless. Identify the side of the specimen for analysis. This is usually the polished side. If the unpolished side is to be analysed, this International Standard is not applicable. If the specimen is too large for insertion into the instrument, a smaller portion will need to be cut from it. To do this, material with a (100)-orientated surface may be cut to form a suitably sized rectangular portion by cleavage along (111) planes. In this way, a square of side 10 mm, bounded by <110> directions, may be conveniently produced. For those specimens with a (111)-orientated surface, a similar cleaving along (111) planes forms equilateral triangles, also bounded by <110> directions. Triangle sides of length 15 mm are convenient. The scribing for cleaving often leaves very small fragments of Si on the specimens. These fragments shall, as far as possible, be removed. The cleaning procedure described in 4.1.6 is often found sufficient for this purpose.

NOTE   The <110> directions are usually indicated by flats cut into the sides of (100)- and (111)-orientated wafers.

4.1.5   Analyses show that wafers and many other materials such as metals accumulate organics, hydrocarbons, silanes and phthalates from the environment. During storage of wafers, the thickness of these adsorbed layers increases to around 0,35 nm on the polished surface in normal, uncirculated laboratory air after 100 days, but is kept below 0,2 nm if a wafer container is used that has been kept closed and has not been exposed to excessive heat[4] (i.e. has been kept below ~35 °C). In either case, the specimens should be analysed without cleaning. If, however, there is evidence that they have been contaminated by organic contaminants (e.g. finger grease) or the specimens have been cut to reduce their size, the contamination can be reduced to a thickness of about 0,14 nm by cleaning as described in 4.1.6.

4.1.6   If the specimens require cleaning, immerse them in a cleaned glass container in HPLC (or equivalent) quality (>99,5 %) isopropyl alcohol (IPA) for 16 h (e.g. overnight). The top of the test tube can be conveniently

closed by a piece of clean aluminium foil. Next, remove the liquid, renew the IPA, agitate ultrasonically for 1 min, rinse in fresh IPA and remove the excess liquid using a jet of pure (>99,9 % purity), dry (<0,01 % water) argon or an equivalent rare gas. If IPA is not available, HPLC-quality chloroform or dichloromethane may be used. The specimens are now ready for analysis.

NOTE   The procedure using 16 h immersion in solvent leaves significantly less carbon than a simple ultrasonic rinse.[4]

If HPLC-quality chloroform or dichloromethane is used instead of IPA, the level of carbon remaining is generally about twice as high. However, the amount left depends on how the specimens have been contaminated in the first place. Hence, chloroform and dichloromethane are not recommended unless IPA is unavailable. Note that there are relevant safety requirements in using all solvents. Carbon deposited during any spectroscopic analysis can be crosslinked by the radiation used, forming a tough adherent layer that cannot be removed without compromising the oxide integrity. Do not use other cleaning methods, even if they are known to remove contamination, since they might also change the oxide thickness[4].

If pure, dry argon or another rare gas is not available, do not use gas from pressurized cans that include a propellant or from compressed-air lines, as these might deposit contaminants. Under no circumstances use any proprietary cleaning agents or liquids containing surfactants.

4.2   Mounting the specimen

Mount the specimen on the specimen holder using fixing screws, or other metallic means, to ensure electrical contact. Do not use double-sided adhesive tape. The (100)-surface specimens shall be mounted such that the photoelectron angle of emission is set in the azimuth at 22,5° to one edge of the rectangular specimens and the (111)-surface specimens shall be mounted such that the angle of emission is in an azimuth of one edge of the triangular specimens. Set these azimuthal angles as accurately as possible and within 2° of their nominal values. This is shown in Figure 2.

NOTE   The reasons for selecting this geometry are described in detail in Reference [5]. This geometry sets the emission direction as a single direction available to both the (100) and the (111) surfaces that is as far from any low index directions as possible. In this direction, the Si substrate forward-focussed intensity is avoided.

4.3   Choosing spectrometer settings

4.3.1   Achieve a good high vacuum with a pressure of less than 5×10^{-9} mbar. Operate the instrument in accordance with the manufacturer's documented instructions. The instrument shall have fully cooled following any bakeout. Select the X-ray source. If a twin-anode source is available, it is usually best to use the Mg anode, rather than the Al anode, since the former gives higher intensity and better energy resolution. If the instrument is not equipped with a twin-anode source or if the monochromated source delivers more intense spectra than the twin-anode source, then use the monochromated source. Ensure that the operation is within the manufacturer's recommended ranges for source power, counting rates, spectrometer scan rate and any other parameter specified by the manufacturer. Ensure that the entrance solid angle for the spectrometer is set at a cone semi-angle of less than 6°. Setting too small an entrance angle will limit the signal quality and the ultimate accuracy of the measurement. Record a survey (widescan) spectrum to ensure that the only significant peaks are those of Si, O and C. The intensity for peaks for all other elements shall not exceed 5 % of the intensity of the Si 2p peak for the uncertainty analysis in 4.7 to be valid. Ensure that there are no significant peaks that are characteristic of the specimen holder. Figure 3 shows an example of a widescan spectrum.

NOTE 1   The peaks visible should be the C 1s, O 1s and O Auger peaks and the Si 2p and 2s peaks. For good practice, the height of the C 1s peak should be less than 30 % of the Si 2s or 2p peak heights although, even for significantly larger amounts of carbonaceous contamination, the measurement should not be affected[5], except to the extent that the important Si 2p signal intensity will be reduced, leading to an increase in the measurement uncertainty. Figure 3 shows a typical result for a cleaned, but stored, specimen.
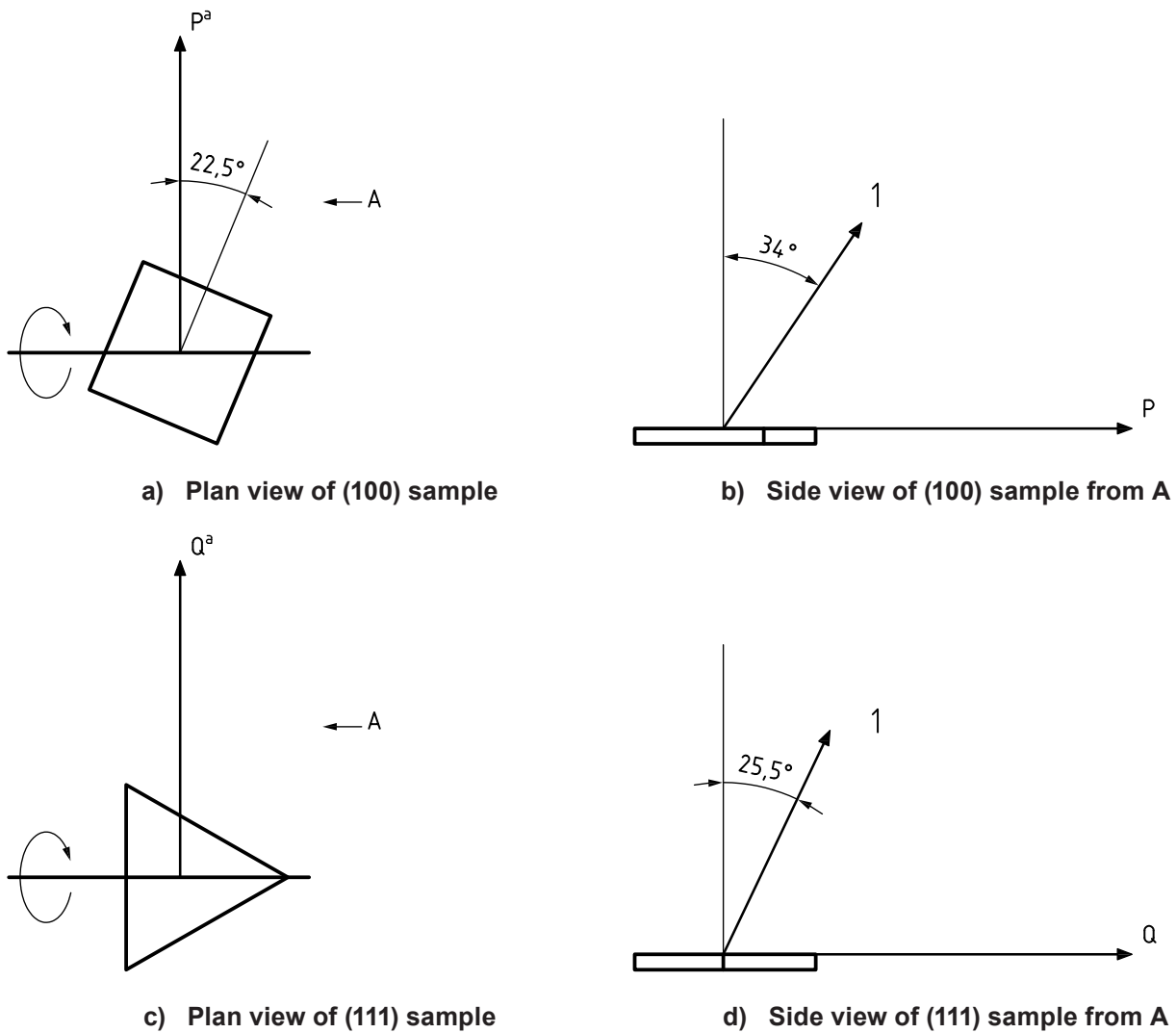
NOTE 2   The higher signal level for the unmonochromated Mg X-rays, compared with that for the monochromated Al X-rays available in many instruments, is important in improving the accuracy of the final result. This choice leads to a reduction in the term U_n discussed later.

4.3.2   Select slit width and pass energy settings to provide peak widths of around 0,6 eV to 0,9 eV for the Si $2p_{3/2}$ and $2p_{1/2}$ elemental peaks.

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4.3.3   For (100) specimens, set the photoelectron angle of emission to 34° and, for (111) specimens, 25,5°.

It has been found that the accuracy in setting this angle can limit the final accuracy of the thickness measurement. It is recommended that users check that the calibration of the angle of emission setting is adequate for their purpose. This can be done conveniently in spectrometers with suitable viewing windows by using a laser beam, reflectors on the specimen stage and standard geometrical relationships[1][2].

NOTE   It could be thought that normal emission is less sensitive to the accuracy of the emission angle. However, the forward focussing along the crystal axis leads to non-linearity in the equations to be used, resulting in significant errors.[5]

a) **Plan view of (100) sample**

b) **Side view of (100) sample from A**

c) **Plan view of (111) sample**

d) **Side view of (111) sample from A**

Key

1   to analyser

a   Analyser azimuth.

Figure 2 — Orientation of the specimens on the specimen stage
[Figures 2 a) and 2 b) show (100) surfaces with the photoelectron angle of emission at 34° from the surface normal and with the analyser set in the azimuth P of the square Si specimen that is in its surface and at 22,5° to the direction of one of the edges. Figures 2 c) and 2 d) show (111) surfaces with the angle of emission at 25,5° from the surface normal and with the analyser set in the azimuth Q of the triangular Si specimen that is in its surface and parallel to the direction of one of the edges.]
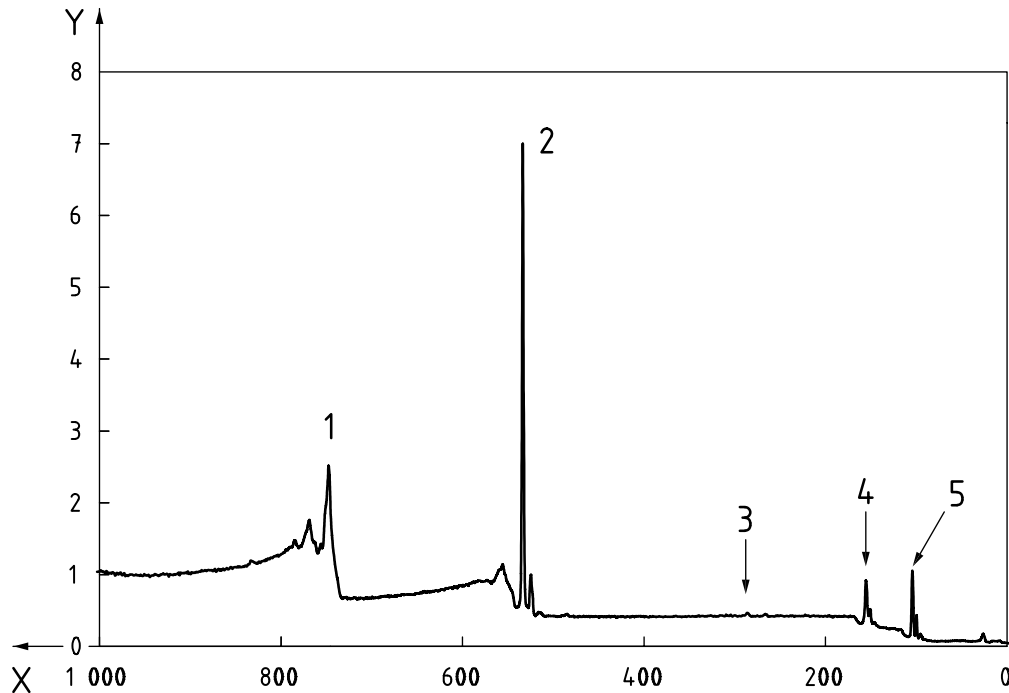
Key

X   binding energy

Y   intensity/10^4 counts

1   oxygen Auger

2   oxygen 1s

3   carbon 1s

4   silicon 2s

5   silicon 2p

**Figure 3 — Widescan (survey) spectrum of SiO$_2$ on Si using Mg Kα X-rays
and before removal of the X-ray satellites**

4.4   Recording data

Record the region of the Si 2p peaks, using the spectrometer settings selected in 4.3.1. If the instrument incorporates a functioning twin-anode source with both Mg and Al X-rays, choose the Mg source, as it gives the higher intensity and better energy resolution. For an unmonochromated source, record from a binding energy 8 eV lower than that of the elemental Si 2p peak at approximately 99,3 eV binding energy to a binding energy 7 eV higher than that peak. For a monochromated Al Ka source, the lower binding-energy limit may be reduced from 8 eV to 3 eV. Note that the accuracy that can be achieved depends on the total signal level measured for the Si 2p peaks. This signal level depends on the product of the count rates in the spectrum and the time for recording that spectrum. For higher accuracy, use longer times. A spectrum acquisition time of 5 min to 10 min is often used. Longer times will improve the accuracy, but any improvement might not be significant unless full consideration is given to all the uncertainties discussed in 4.7 to ensure that other uncertainties do not dominate the total uncertainty. The effects of drift in any of the spectrometer properties can be reduced by acquiring the data using several scans that are added, rather than one single scan.

NOTE   Examples of uncertainties associated with different signal levels are described in Reference [6].

4.5   Measuring intensities

4.5.1   In this subclause, all intensities are measured as peak areas by peak fitting. The mathematical symbols in all equations relate to these peak area measurements.

4.5.2   For data recorded with an unmonochromated X-ray source, use appropriate software to remove the X-ray satellites. It is important to do this first in order to obtain flat backgrounds in the relevant energy regions to fit the Shirley background. The end points for the Shirley background are important and shall be in the flat regions at higher and lower energy than the 2p peaks. In some software systems, the ordinate values of the Shirley background end points can be set by averaging over a number of energy channels (e.g. 21 channels). This leads to improved precision.[6] In this case, all of the averaged end points shall be in the above flat regions. In Si, the 2p peak is split into two components, called $2p_{1/2}$ and $2p_{3/2}$, with peak area intensities in the ratio of 1 to 2. This effect is called spin-orbit splitting. These peaks are separated by 0,6 eV and, if unresolved, lead to significant asymmetry in the narrow elemental peak but not in the broader oxide peak. Two methods of treating spin-orbit splitting are described below. If high-accuracy thicknesses are required, go to 4.5.3. If a simpler, faster, but less accurate procedure, with thicknesses limited to 2 % accuracy, is required, go to 4.5.5.

NOTE   The Shirley and other backgrounds are discussed in ISO/TR 18392[7]. The Shirley background is used here since the uncertainties are only evaluated for that background.

4.5.3   Next, for high-accuracy thicknesses, if spin-orbit subtraction software that will remove 50 % of the intensity at a 0,6 eV higher binding energy at each position is available, use it to remove the spin-orbit contribution and simplify the spectrum. Unfortunately, this software is often not available. In that case, go directly to 4.5.4. If the spin-orbit contribution has been removed, using peak synthesis software with each peak component described by either a sum or a product of a Gaussian and a Lorentzian lineshape function, fit the spectrum to five peaks with a Shirley background. An example of such a fitted spectrum is shown in Figure 4 a). The five peaks have been assigned as follows:

— a peak arising from the elemental Si substrate, intensity I_{Si};

— a peak from an interfacial oxide, Si_2O, intensity I_{Si_2O}, at a binding energy 0,95 eV higher than that of the first peak;

— a peak from a second interfacial oxide, SiO, intensity I_{SiO}, at a binding energy 1,75 eV higher than that of the first peak;

— a peak from a third interfacial oxide, Si_2O_3, intensity $I_{Si_2O_3}$, at a binding energy 2,48 eV higher than that of the first peak;

— a peak from the dioxide, SiO_2, intensity I_{SiO_2}, at a binding energy 3,8 eV to 4,3 eV higher than that of the first peak.

For convenience, these shifts and suggested limits for fitting the peak full widths at half maximum intensity (FWHMs) are listed in Table 1. Record the intensities of the five peaks and go to 4.6.

NOTE 1   The intermediate and dioxide peak positions are as originally defined by Hollinger and Himpsel[8] and by Keister *et al*[9] and are as used by Seah and Spencer[5] and by Seah *et al*[10][11].

The majority of commercial XPS instruments have available peak functions in which each peak component is described by a sum or a product of a Gaussian and a Lorentzian lineshape function,[12] where the widths, total intensity and mixing proportions are adjusted to optimize the fit. Both lineshapes give equivalently accurate results for this work. Other lineshapes, such as Doniach-Šunjić or polynomials, shall not be used.

NOTE 2   The FWHM upper limits are useful to restrict the fits for the weak interfacial oxides to physically realistic results.
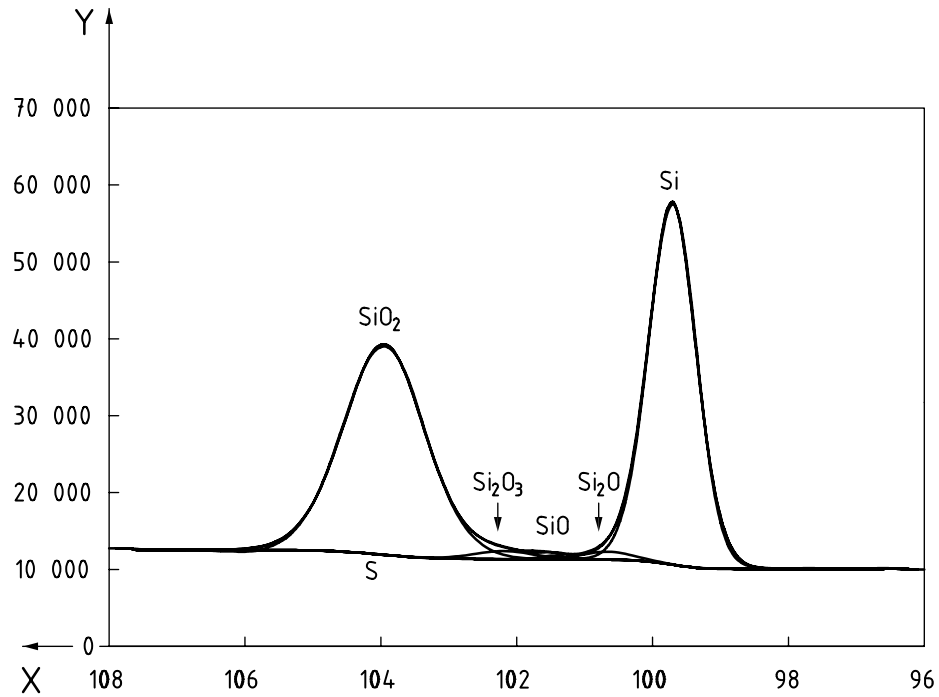
a) **Five peaks after spin-orbit subtraction**
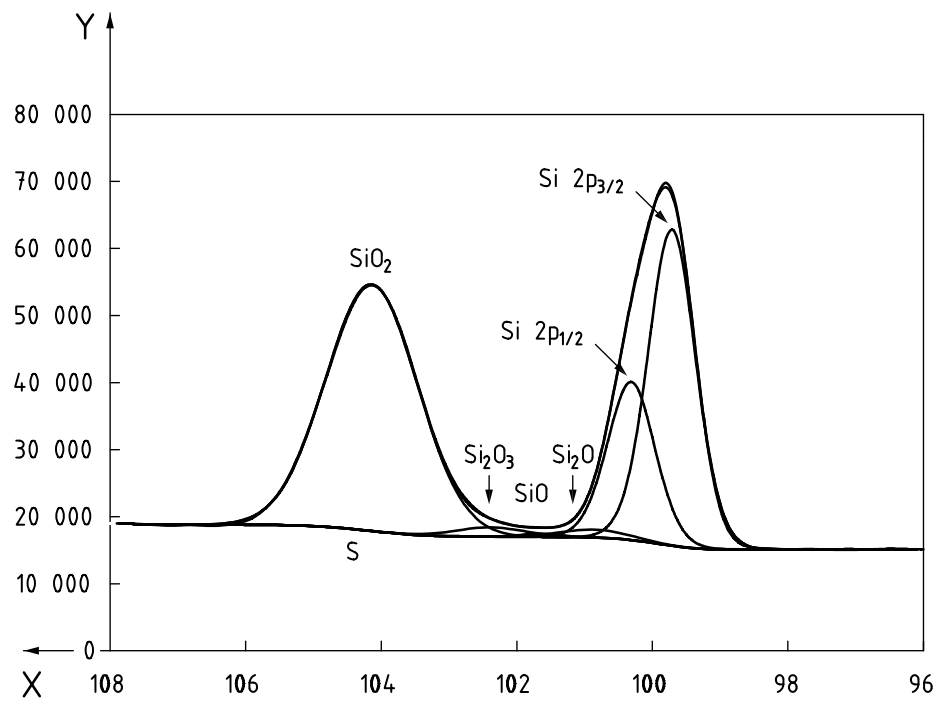
b) **Six peaks without spin-orbit subtraction**

Key

X   binding energy (eV)

Y   intensity (counts)

Figure 4 — Peaks with fitted components for SiO$_2$ on Si

[The spectrum is for an Mg X-ray source at 0,1 eV abscissa intervals and has the X-ray satellites removed. Figure 4 a) is for five peaks after spin-orbit subtraction and Figure 4 b) for six peaks without spin-orbit subtraction. In both cases, the end points for the Shirley background (S) are averaged over 21 points.]

Table 1 — Values, in eV, of the oxide binding-energy shifts to higher energies from the Si 2p$_{3/2}$ elemental peak, and suggested peak FWHM limits

Peak	Five-peak method eV	Six-peak method eV	FWHM upper limit eV
SiO$_2$	3,8 to 4,3	4,0 to 4,5	1,5
Si$_2$O$_3$	2,48	2,68	1,5
SiO	1,75	1,95	1,5
Si$_2$O	0,95	1,15	1,7
NOTE The SiO$_2$ values in columns 2 and 3 are given as an energy range since SiO$_2$ is an insulator. It can therefore charge and the peak moves slightly on the binding-energy scale, but the extent of charge depends on the instrument and the oxide thickness.[13]			

4.5.4   If spin-orbit subtraction software is not available, use the peak synthesis software with each peak component described by either a sum or a product of a Gaussian and a Lorentzian lineshape function to fit the spectrum to six peaks with a Shirley background. An example of such a fitted spectrum is shown in Figure 4 b). The six peaks have been assigned as follows:

— firstly, there are two peaks arising from the elemental Si substrate, one peak having an intensity which is 50 % of that of the other and being at a 0,6 eV higher binding energy, the total intensity being I_{Si};

— next is a peak from an interfacial oxide, Si$_2$O, intensity I_{Si_2O}, at a binding energy 1,15 eV higher than that of the first peak;

— this is followed by a peak from a second interfacial oxide, SiO, intensity I_{SiO}, at a binding energy 1,95 eV higher than that of the first peak;

— a peak from a third interfacial oxide Si$_2$O$_3$, intensity $I_{Si_2O_3}$, at a binding energy 2,68 eV higher than that of the first peak;

— and a peak from the interfacial dioxide, SiO$_2$, intensity I_{SiO_2}, at a binding energy 4,0 eV to 4,5 eV higher than that of the first peak.

For convenience, these shifts and suggested peak full widths at half maximum intensity (FWHM) upper limits are listed in Table 1. Record the intensities of the six peaks and go to 4.6.

NOTE 1   The peak positions here are 0,2 eV further from the Si 2p$_{3/2}$ peak than in 4.5.3.

The majority of commercial XPS instruments have available peak functions in which each peak component is described by a sum or a product of a Gaussian and a Lorentzian lineshape function,[12] where the widths, total intensity and mixing proportions are adjusted to optimize the fit. Both lineshapes give equivalently accurate results for this work. Other lineshapes, such as Doniach-Šunjić or polynomials, shall not be used.

NOTE 2   The FWHM upper limits are useful to restrict the fits for the weak interfacial oxides to physically realistic results.

4.5.5   This subclause describes a simpler procedure that gives thicknesses of good, but poorer, accuracies. If spin-orbit subtraction software that will remove 50 % of the intensity at 0,6 eV higher binding energy at each position is available, use it to remove the spin-orbit contribution and simplify the spectrum. If this software is not available, go to 4.5.6. Next, using peak synthesis software with each peak component described by either a sum or a product of a Gaussian and a Lorentzian lineshape function, fit the spectrum to two peaks with a Shirley background. The two peaks have been assigned as follows:

— a peak arising from the elemental Si substrate, intensity I_{Si};

— a peak from the dioxide, SiO$_2$, intensity I_{SiO_2}, at a binding energy 3,8 eV to 4,3 eV higher than that of the first peak.

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Record the intensities of the two peaks and go to 4.6.

The majority of commercial XPS instruments have available peak functions in which each peak component is described by a sum or a product of a Gaussian and a Lorentzian lineshape function,[12] where the widths, total intensity and mixing proportions are adjusted to optimize the fit. Both lineshapes give equivalently accurate results for this work. Other lineshapes, such as Doniach-Šunjić or polynomials, shall not be used.

4.5.6   If spin-orbit subtraction software is not available, use the peak synthesis software with each peak component described by either a sum or a product of a Gaussian and a Lorentzian lineshape function to fit the spectrum to three peaks with a Shirley background. The three peaks have been assigned as follows:

— firstly, there are two peaks arising from the elemental Si substrate, one peak having an intensity which is 50 % of that of the other and being at a 0,6 eV higher binding energy, the total intensity being I_{Si};

— the third peak is from the dioxide, SiO_2, intensity I_{SiO_2}, at a binding energy 4,0 eV to 4,5 eV higher than that of the first peak.

Record the intensities of the three peaks and go to 4.6.

The majority of commercial XPS instruments have available peak functions in which each peak component is described by a sum or a product of a Gaussian and a Lorentzian lineshape function,[12] where the widths, total intensity and mixing proportions are adjusted to optimize the fit. Both lineshapes give equivalently accurate results for this work. Other lineshapes, such as Doniach-Šunjić or polynomials, shall not be used.

4.6   Calculating the oxide thickness

4.6.1   If five or six peaks have been measured for high-accuracy thicknesses, go to 4.6.2. If two or three peaks have been measured for a more rapid, but less accurate, analysis, go to 4.6.3.

4.6.2   For high-accuracy thicknesses, with both the method using five peaks and that using six peaks in which the two elemental Si 2p spin-orbit contributions (Si $2p_{3/2}$ and Si $2p_{1/2}$) are summed into I_{Si}, first calculate the thickness of the component oxides, as follows:

$$d_{SiO_2} = L_{SiO_2} \cos\theta \ \ln\left[1 + \frac{\left(\dfrac{I_{SiO_2}}{R_{SiO_2}}\right)}{\left(\dfrac{I_{Si_2O_3}}{R_{Si_2O_3}} + \dfrac{I_{SiO}}{R_{SiO}} + \dfrac{I_{Si_2O}}{R_{Si_2O}} + I_{Si}\right)} \right] \tag{1}$$

$$d_{Si_2O_3} = L_{Si_2O_3} \cos\theta \ \ln\left[1 + \left(\frac{I_{Si_2O_3}}{R_{Si_2O_3} \, I_{Si}}\right) \right] \tag{2}$$

$$d_{SiO} = L_{SiO} \cos\theta \ \ln\left[1 + \left(\frac{I_{SiO}}{R_{SiO} \, I_{Si}}\right) \right] \tag{3}$$

and

$$d_{Si_2O} = L_{Si_2O} \cos\theta \ \ln\left[1 + \left(\frac{I_{Si_2O}}{R_{Si_2O} \, I_{Si}}\right) \right] \tag{4}$$

where the values of $L_{Si_2O_x}$ and $R_{Si_2O_x}$ are generated by linear interpolation between the values for SiO_2 and Si, depending on the value of x, as shown in Table 2 for both Mg and Al Kα X-rays.

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Table 2 — Values of $L_{\mathrm{Si_2O}_x}$ and $R_{\mathrm{Si_2O}_x}$ for the five peaks[1][14]

Peak	x-value	Mg Kα X-rays		Al Kα X-rays	
		$L_{\mathrm{Si_2O}_x}$ (nm)	$R_{\mathrm{Si_2O}_x}$	$L_{\mathrm{Si_2O}_x}$ (nm)	$R_{\mathrm{Si_2O}_x}$
SiO_2	4	2,996 0	0,932 9	3,485 0	0,932 9
Si_2O_3	3	2,850 8	0,949 7	3,217 5	0,949 7
SiO	2	2,705 5	0,966 5	2,950 0	0,966 5
Si_2O	1	2,560 3	0,983 2	2,682 5	0,983 2
Si	0	2,415 0	1,000 0	2,415 0	1,000 0

These thicknesses are then summed to give the effective oxide thickness, using the relationship

$$d_{\mathrm{oxide}} = d_{\mathrm{SiO_2}} + 0{,}75\, d_{\mathrm{Si_2O_3}} + 0{,}5\, d_{\mathrm{SiO}} + 0{,}25\, d_{\mathrm{Si_2O}} \tag{5}$$

which apportions the thickness according to the oxygen content.

To calculate the uncertainty in this thickness, go to 4.7.

4.6.3 For lower-accuracy thicknesses, with both the method using two peaks and that using three peaks in which the two Si 2p elemental contributions are summed into I_{Si}, calculate the oxide thickness as follows:

$$d_{\mathrm{SiO_2}} = L_{\mathrm{SiO_2}} \cos\theta \ln\left[1 + \left(\frac{I_{\mathrm{SiO_2}}}{R_{\mathrm{SiO_2}} I_{\mathrm{Si}}} \right) \right] \tag{6}$$

where the relevant parameters are given in the top data line of Table 2.

To calculate the uncertainty in this thickness, go to 4.7.

NOTE In References [5] and [10], it was noted that the three interfacial oxides contributed a thickness of $(0{,}128 \pm 0{,}008)$ nm, close to the estimated 0,124 nm for an ideal interface.[5] The use of the simpler Equation (6), instead of Equations (1) to (5), does not simply give a difference of 0,128 nm since the fitting procedure for two peaks leads to a value of $I_{\mathrm{SiO_2}}$ slightly higher than that obtained when five peaks are used. The ratio of the thickness obtained using Equation (6) to that obtained using Equations (1) to (5) is within 1,5 %,[14] a difference significantly smaller than the 0,128 nm above.

4.7 Calculating the uncertainty of the oxide thickness

4.7.1 The uncertainty, U, of the silicon oxide thickness derived from Equations (5) and (6) at the 95 % level of confidence can be calculated from the following equation:[6][14]

$$U^2 = U_{\mathrm{n}}^2 + U_\theta^2 + U_{\mathrm{A}}^2 + U_{\mathrm{E}}^2 + U_{\mathrm{F}}^2 + U_{\mathrm{L}}^2 \tag{7}$$

where U_{n}, U_θ and U_{A} are the uncertainty contributions, for a 95 % confidence interval, to the spectrum measurement statistics for the measured Si 2p spectrum, the angle setting and the analyser electron optics defining the solid angle of acceptance, respectively. The term U_{E} allows for the contribution from the uncertainty

of the validity of the equations for thicknesses below 8 nm. The term U_F allows for the uncertainty in using Equation (6) instead of Equation (5). U_L is the uncertainty in the attenuation length.

NOTE   For most of the work required here, it is often suitable to calculate the expanded uncertainties from measured standard deviations with the expansion as described in textbooks and in Annex G of ISO/IEC Guide 98-3:2008[15]. This expansion uses the factors given as the critical values of Student's t-distribution with a known number of degrees of freedom. The degrees of freedom are one less than the number of independent observations of the value considered. The values tabled can be for a one-sided distribution, where the probability sought is 0,05, or for a two-sided distribution, where the probability sought for exceeding the critical value given is 0,025. A convenient table for a two-sided distribution can be found in Reference [16].

4.7.2   The value of U_n will depend on the instrument and the operating conditions. It can be determined for each specimen by calculating several measures for d_{oxide} for that specimen for independent measurements of the Si 2p spectrum, resetting the specimen position each time, and by determining the standard deviation of the associated random scatter. U_n is then calculated by expansion in the usual way. This value will be reduced by increasing the signal level, but not if this also degrades the energy resolution to broader than about 0,9 eV. U_n tends to be significantly higher if the X-ray source is monochromatic Al Kα rather than unmonochromated Mg Kα, as a result of the significantly lower count rates with the former. If only one specimen is to be analysed to estimate U_n for other specimens, this shall be carried for the specimen with the thickest oxide layer, but this thickness shall be no greater than 8 nm.

NOTE U_n generally increases monotonically with d_{oxide}.[6]

4.7.3   The value of U_θ might be different for the (100) and the (111) specimens. This difference arises from the uncertainty in θ which, in turn, has a type A contribution from the precision of setting θ and a type B contribution concerning the accuracy of the angle calibration. Careful calibration of the spectrometer can limit the uncertainty in θ to less than 0,25°[6] whereas, for instruments as supplied by a manufacturer, this uncertainty can be 2,5°.[2] [17] An uncertainty of 1° in θ leads to a value for U_θ of 1,2 % for (100) specimens and 0,8 % for (111) specimens.

4.7.4   The value of U_A depends on the solid angle of acceptance of the spectrometer.[6] For spectrometers with a cone semi-angle of 6° or less, this contribution is small and can generally be ignored.

4.7.5   The value of U_E is the same for all instruments. Studies have shown that U_E is less than 0,025 nm[14] [17] for the specimen geometries and intensity-measurement procedures described here.

4.7.6   The value of U_F may be ignored for the higher-accuracy five- or six-peak methods, but is 1,5 %[6] for the thickness range 1,5 nm to 8 nm when using the faster, but less accurate, two- or three-peak methods.

4.7.7   If R_{SiO_2} is taken as 0,932 9, then U_L, determined in Reference [5], is 0,010 7d at an expansion of $k = 2$ for L_{SiO_2} taken as 2,996 nm or 3,485 nm for Mg or Al Kα X-rays, respectively.[17] The uncertainties in $R_{Si_2O_x}$ are accommodated in this expression.

NOTE   Typical values of U for instruments under good control and using the five- or six-peak methods range from 0,05 nm at $d_{oxide} = 1,5$ nm to 0,2 nm at $d_{oxide} = 8$ nm.[11] For the two- or three-peak methods, these uncertainties increase to approximately 0,055 nm and 0,25 nm, respectively.

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