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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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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.

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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

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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_{Si_2O} attenuation length for Si 2p electrons in Si_2O

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

$L_{Si_2O_3}$ attenuation length for Si 2p electrons in Si_2O_3

L_{SiO_2} attenuation length for Si 2p electrons in SiO_2

R_{Si_2O} intensity normalization parameter for the Si_2O contribution to the Si 2p peak

R_{SiO} intensity normalization parameter for the SiO contribution to the Si 2p peak

$R_{Si_2O_3}$ intensity normalization parameter for the Si_2O_3 contribution to the Si 2p peak

R_{SiO_2} intensity normalization parameter for the 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

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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

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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.

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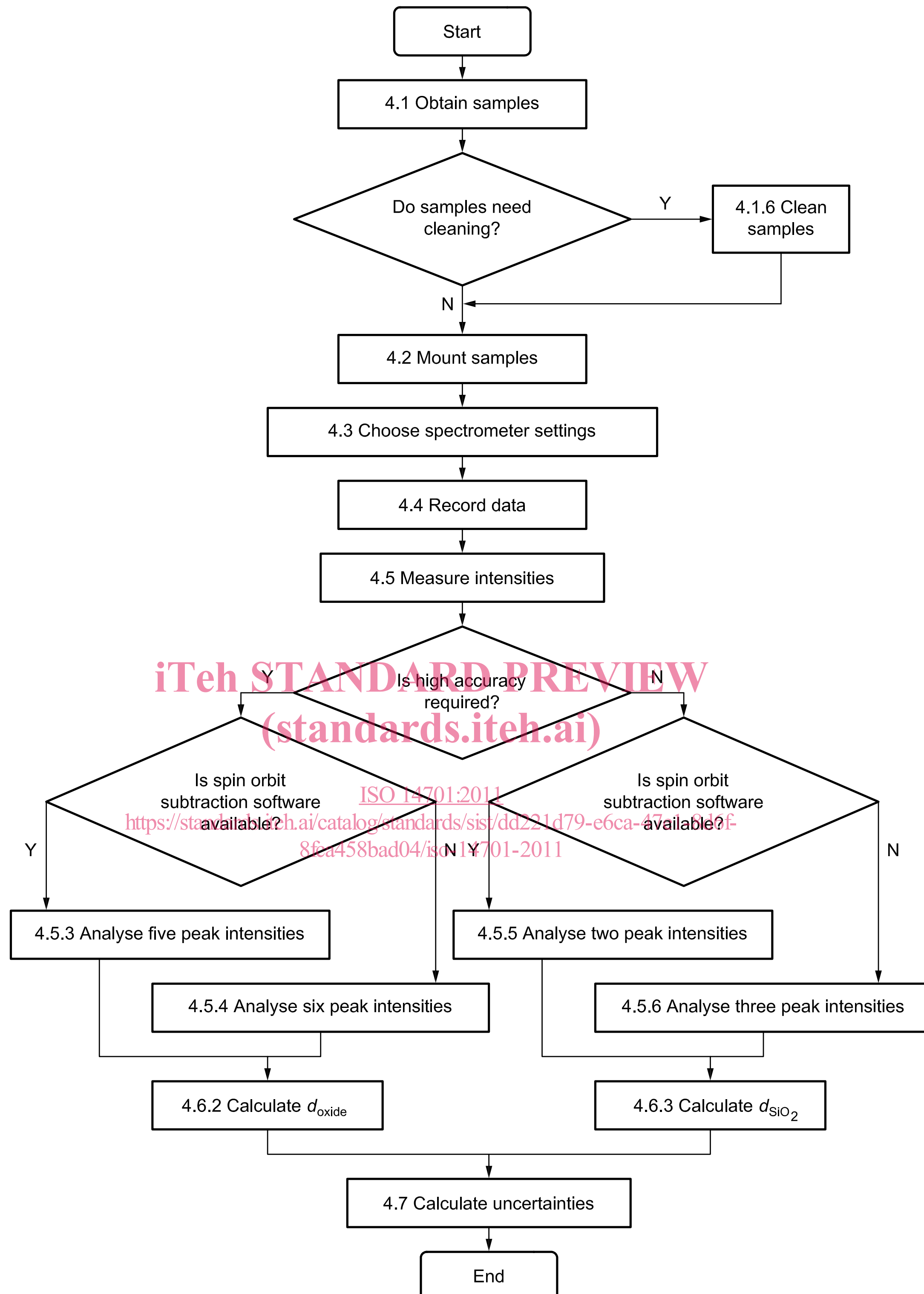

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Figure 1 — Flowchart of the measurement process
(Y and N at decision points are the usual “yes” and “no”, respectively)

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].

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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.

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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

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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.

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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.

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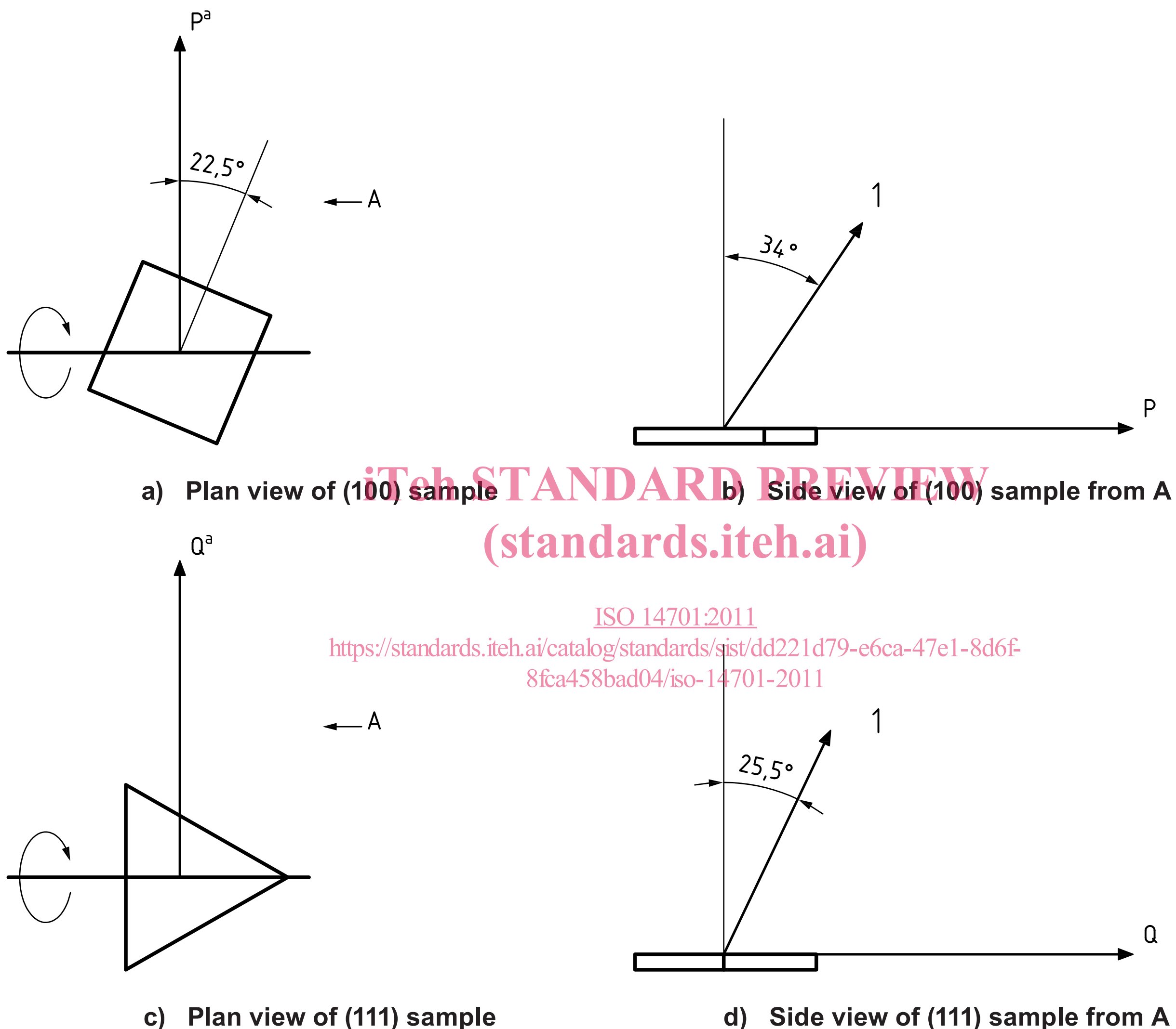
4.3.3 For (100) specimens, set the photoelectron angle of emission to 34° and, for (111) specimens, 25,5°.

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

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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.]

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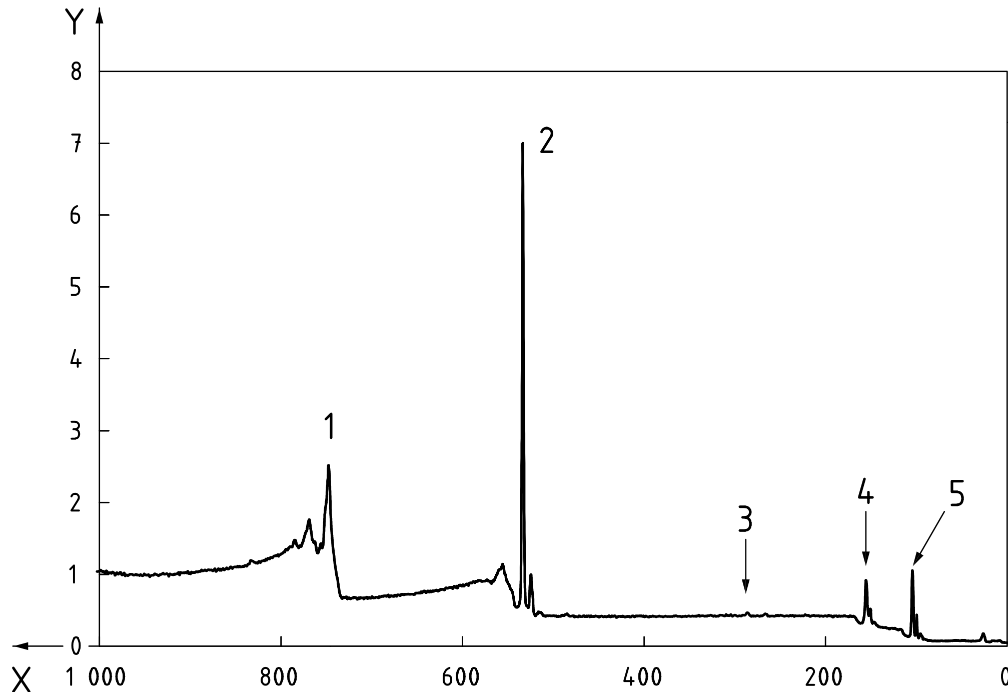

Key

X binding energy

Y intensity/10^4 counts

1 oxygen Auger

2 oxygen 1s

3 carbon 1s

4 silicon 2s

5 silicon 2p

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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.

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