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Review

Recent Advances to Establish XPS as an Accurate Metrology Tool

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A brief review is given of the project to measure the thickness of SiO_2 on Si in the range 1.5 nm to 8 nm by XPS. An outline is provided for the rationale of the work and the way that progress was organised to achieve accuracy better than 1%. Key elements of the uncertainty that needed addressing were the establishment of a reference geometry to avoid forward focusing from the single crystal silicon substrate, adequate signal strength to reduce the signal uncertainty, sufficient angular acceptance in the analyser to average the remaining forward focusing structure but not so large as to cause a bias, and accurate setting of the angle of emission for the reference geometry. With these parameters controlled, XPS becomes a linear and repeatable method for determining the thickness of SiO_2 on Si. By measuring the difference in thicknesses of a series of films against one or more other methods such as ellipsometry, X-ray reflectance, neutron reflectance, etc, the relevant attenuation lengths may be determined, thus converting XPS from a precise method into an accurate and traceable method. This general procedure can be used for any material layer. Details are given that led to a final result with a standard uncertainty better than 1%.

1. Introduction

XPS is a powerful method for analysing materials at surfaces and, of the surface specific methods, is probably the most quantitative. However, for general quantification, it is known that the uncertainty in the general prediction of the inelastic mean free paths [1] involved is typically 17.4%. Additional uncertainties of 10% arise from sensitivity factors [2] and further problems arise from the elastic scattering contributions that lead to the simple linear equations used by analysts being only approximately valid.

Nevertheless, for the outermost 10 nm of a surface and from the points of view of chemical state and quantification, XPS is generally one of the best of the analytical methods that are available in laboratories. Therefore, it was decided in 2002 to evaluate both the precision and accuracy attainable by XPS and other methods. In improving the accuracy of XPS to better than 20%, clearly the relevant electron attenuation lengths would need determination.

These requirements coincided with the reduction in the thickness of gate oxides for microelectronic devices such that it became clear that the system to study would be SiO_2 on Si. There was a large volume of helpful data for this system and many analysts had experience in measuring the thickness by a variety of methods. Since the work had a focus on accuracy rather than precision, it was clear that the National Metrology Institutes (NMIs) should have a major contribution but it was also clear that major expertise would also reside in the laboratories of the microelectronics manufacturers and in University Departments with allied interests. The NMI focus led to the setting up of a pilot study under a Consultative Committee for Amount of Substance (CCQM) [3], amount of substance being its core issue. Such pilot studies may involve any laboratory with relevant expertise in addition to NMIs.

At that time, results of SiO_2 thickness measurements were reported of the range of data that would be found by analysts using different methods [4]. The standard deviations for data for thicknesses below 4 nm were greater than 50%. On the other hand, the International Technology Roadmap for Semiconductors (ITRS) indicated that 4% uncertainty at 3 standard deviations was needed [5]. It was not clear at that time if the gap could be adequately closed with XPS or indeed with any other method. We now know that it can be. The route to achieving 1% standard uncertainty is split over a number of publications and it is helpful to establish here the salient points. The work progressed in a number of stages.

2. Preparation and cleaning of the samples

The first issue in the study was to ensure that samples that were made could be transported to laboratories for analysis without significant contamination and without change in the oxide thickness. Thus, in 2002, the rates of contamina-

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tion for samples held in different containers were evaluated as well as simple methods of cleaning that were not likely to change the oxide thickness [6]. It was found that glass, polypropylene and polyethylene containers were all adequate and that cleaning was relatively straightforward using isopropyl alcohol [6].

For XPS studies, extra cleaning was shown to be unnecessary. The analysis method was based on the measurement of the Si 2p peak areas in the elemental, I_e, and oxide, I_o, states as shown by the peaks designated "Si" and "SiO_2", respectively, in Fig 1(b). These Si 2p peaks are shown in context in the widescan spectrum of Fig 1 (a). The thickness was calculated from the equation [7]

$$d = L \cos \theta \ln (1 + R/R_o) \quad (1)$$

where L is the attenuation length of the electrons in SiO_2, θ is the angle of emission from the surface normal as shown in Fig 2, R is the measured ratio of I_o/I_e, and R_o is the similar ratio for the bulk oxide and bulk element. Since the peaks for I_o and I_e are very close in energy, any contamination is expected to reduce both intensities equally. This was verified, experimentally, over a contamination range that was an order of magnitude more than required, showing that the contamination could be ignored [7].

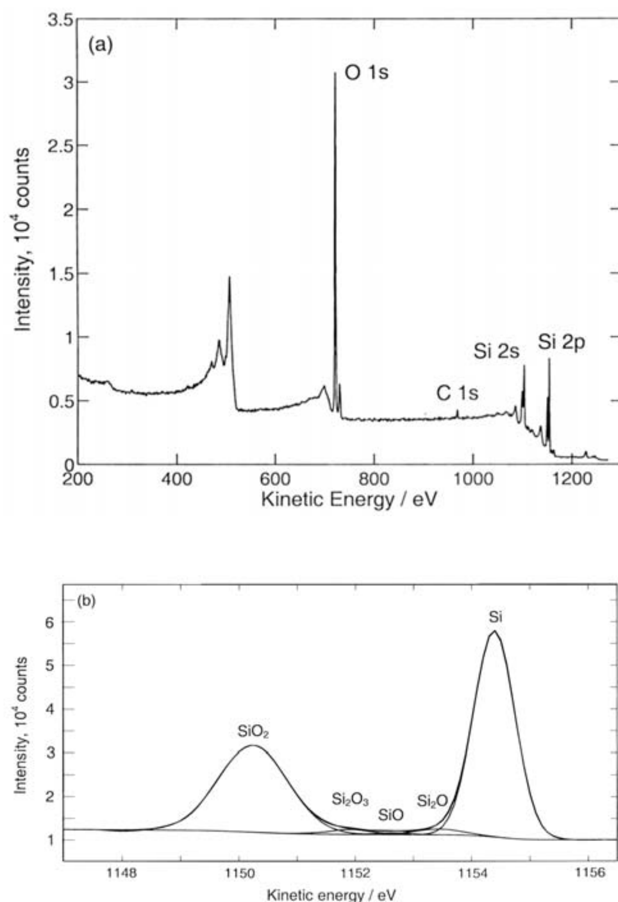

Fig. 1 XPS data for a sample with ~2 nm of oxide, cleaned as described in the text, using Mg X-rays with an analyser resolution of 0.4 eV: (a) widescan; (b) the Si 2p peaks after satellite and spin-orbit splitting removal, showing the Shirley background and the peak synthesis, after Seah and Spencer [7].

In order to ensure that the samples were repeatable and reliable, thermal oxides were used rather than plasma deposited oxides and samples were obtained from two pilot scale facilities; one in Europe and one in the US. These included both (100) and (111) wafers to ensure that analytical methods led to consistency for different crystal orientations. Although semiconductor manufacture is mainly based on (100) Si, there is interest in the Avogadro project [8,9] for all orientations. In order to ensure that the different wafer samples that were studied were equivalent, all samples were mapped by ellipsometry within a dust-free environment soon after manufacture. A map of a rejected wafer is shown in reference [10]. These maps have a measurement precision of 2 pm [10,11] and allow areas consistent within 1% to be selected for intercomparisons. Analysis of sets of samples showed an average change in thickness over a period of 6 months of 0.001 ± 0.019 nm [11]. In this text, where scatters or uncertainties are described or follow the "±" symbol, the standard deviations or standard uncertainties are given unless explicitly defined otherwise. Recent studies show that the above period is actually greater than 3 years and so the thermal oxide samples are very stable.

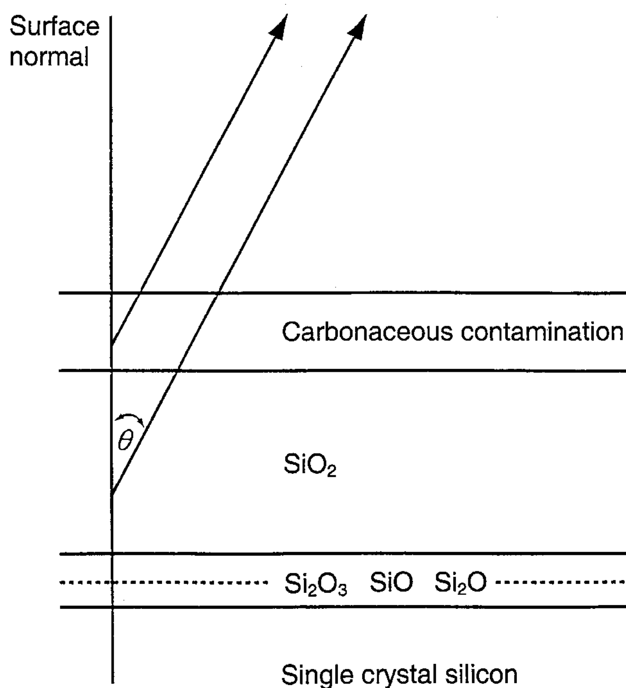

Fig. 2 Schematic of the structure of the contamination and oxide layers analysed, after Seah and Spencer [7].

3. Developing the measurement by XPS

At the start of this work, Eq (1) was reviewed [7]. The value of L could be calculated directly. The value of R_o was calculated to be 0.53 but published experimental data ranged from 0.67 to 0.94. It was concluded that the calculated value would relate to the peak areas following removal of all extrinsic losses. To use this value, the measurements would need to include all intrinsic plasmons, shake-up losses, etc. However, this was not feasible since the losses from the elemental and oxide Si 2p peaks overlapped. The peak areas were actually to be measured using a Shirley [12] background, since this led to the required precision, but this method, unfortunately, ignores all shake-up intensity. Thus, an experimental value of R_o was used rather than the theoretically derived value.

In a detailed analysis of the geometry for the experimental measurements for Eq (1), it was found that effects of forward focusing, established by Mitchell *et al.* [13] were strong, as shown in Fig 3. These effects could lead to reduction in the deduced value for d along the crystal directions by over a range of 40% if L and R_o were assumed to be the same for all geometries. For small aperture spectrometers, a change in emission angle near the [100] pole of 2°, as shown in Fig 3(d), could lead to an apparent change in thickness of 36%! The region giving least variation was emission in the centre of the stereographic triangle, at 25.5° to the surface normal for (111) surfaces and 34° to the surface normal for (100) surfaces. These angles from the surface normal had, of course, to be in defined azimuths along the bisectors of the relevant crystal directions [7]. We called these geometrical settings the reference geometry (RG). If geometries close to or along a low index direction are used, the thicknesses derived from Eq (1) will be too small and may be over-sensitive to the setting of the emission angle of the sample holder stage. The extent to which the thicknesses are too small will not be a constant fraction, applicable to all thicknesses, but will vary with thickness in a non-linear manner. Thus, the correct thicknesses cannot be derived by a simple upward scaling of L [11] and the derivation of an equation to replace Eq (1) for this geometry requires a very much more complex analysis.

As the measurement quality improved, it was decided to include the very small peaks shown in Fig 1 into the quantification [14]. This led to a set of equations of the style of Eq (1) but with a separate equation for each chemical state, Si_2O_x where x = 1, 2, 3 and 4; those for x = 1, 2, and 3 being

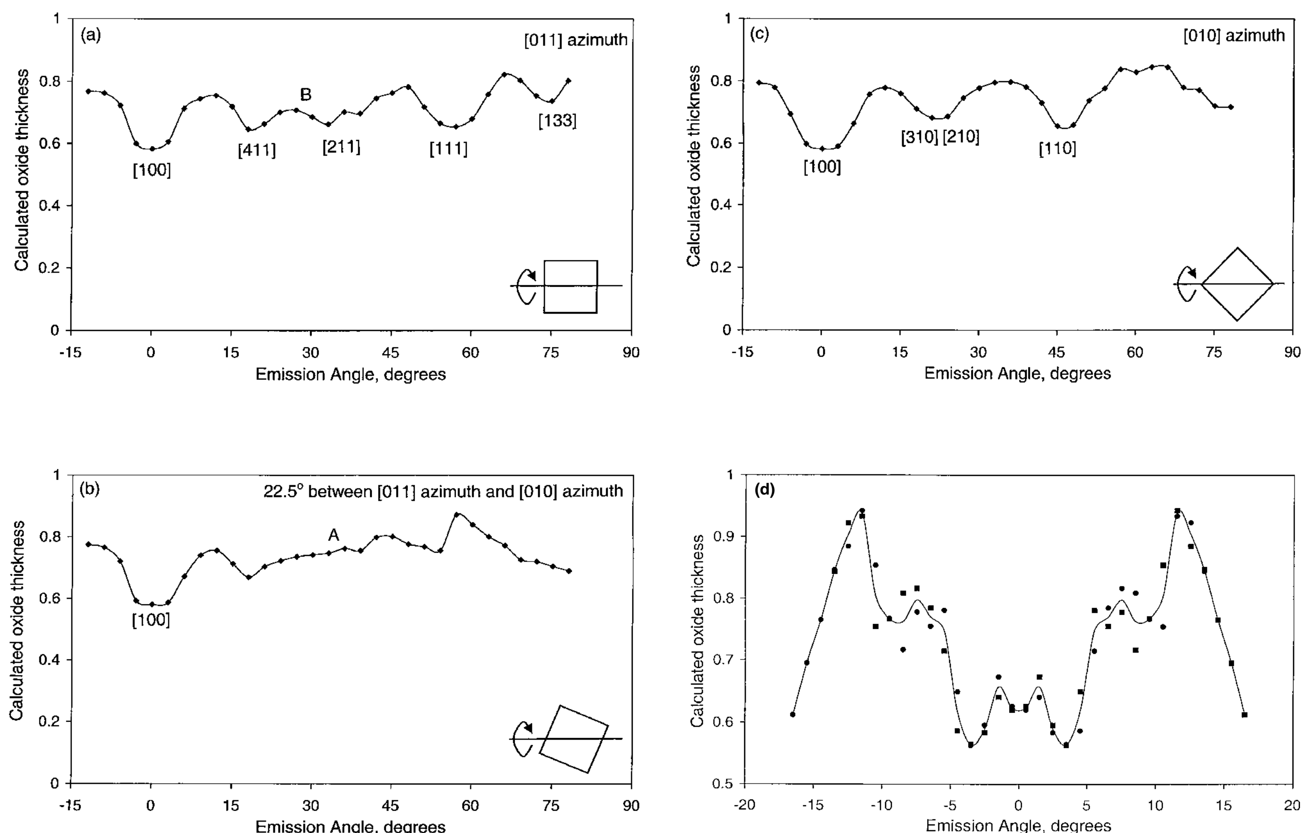

Fig. 3 Calculated oxide thicknesses, nm, for the (100) surface of an ultra-thin oxide wafer from Eq (1) for changes in the angle of emission θ for 3 azimuths: (a) $\phi = 0°$, [011] azimuth; (b) $\phi = 22.5°$; (c) $\phi = 45°$, [010] azimuth; (d) detail around the [100] pole in (a) using a very small acceptance aperture. The crystal directions are noted on the plots. The small symbol in the lower right of the plots shows the axis of rotation in relation to the wafer piece, after Seah and Spencer [7].

like Eq (1) but that for SiO_2 being rather more complex. For these equations, the relevant values of L and R_o were, in each case, linearly interpolated between the values for Si and for SiO_2. The final oxide equivalent thickness was then taken as the sum

$$d = \sum_{n=1}^{4} \left(\frac{x}{4}\right) d_{Si_2O_x} \qquad (2)$$

where each interfacial oxide contributes proportionately with its oxygen content. The total thickness of the interface oxides typically added 0.128 ± 0.008 nm to the SiO_2 thickness, as expected for a near-perfect interface [11]. In this study [14], R_o was evaluated to be 0.9329 for Mg Kα X-rays. The value was, of course, not this accurate but it was known that if d was calibrated, the values for R_o and L were approximately inversely related and that fixing R_o would simply shift all the uncertainty to L. Analyses with Al X-rays showed that if the energy dependence of L between the Si 2p kinetic energy for Mg and Al Kα X-rays was as calculated by Tanuma *et al.* for SiO_2 [15], then the same value of R_o was applicable.

The effects of elastic scattering, in addition to the forward focusing of the substrate intensity, affects the oxide intensity. Although this is largely taken into account in calculating the attenuation length L from the IMFP, it was shown that L depended on the emission angle of the electrons and also the thickness d [16]. Evaluation [14] of Powell and Jablonski's calculations [16] showed that the added non-linearity conveniently minimised in the intermediate emission directions of the reference geometry. The combined uncertainty of this effect and of the use of a single Shirley background was estimated to be within ± 0.025 nm for the thickness range $0.3 \le d \le 8$ nm when using the NPL reference geometry.

4. The CCQM pilot study

The CCQM pilot study was launched in early 2002 and involved 31 laboratories using 10 analytical methods: medium energy ion scattering spectrometry (MEIS), nuclear reaction analysis (NRA), Rutherford backscattering spectrometry (RBS), elastic backscattering spectrometry (EBS), XPS, secondary ion mass spectrometry (SIMS), ellipsometry, grazing incidence X-ray reflectometry (GIXRR), neutron reflectometry (NR) and transmission electron microscopy (TEM). The respondees' data were all analysed using the relation [11]

$$d_{respondee} = md + c \qquad (3)$$

where d was the thickness evaluated by NPL. NPL's original ellipsometry data were evaluated in this way and found to scatter by 0.089 nm around this line with $m = 0.993$ and $c = 0.480$ nm as shown in Fig 4. These values were changed later by a few percent and we shall come to this later. The scatter of 0.089 nm was excellent in view of previous studies but, ideally we may have expected 0.025 nm from the XPS, 0.005 nm from the ellipsometry and around 1% from the repeatability of our XPS as it was at that stage. Thus, a final scatter closer to 0.05 nm was expected. That m was close to unity was a surprise since the value of m depended on the value of the IMFP, with an estimated uncertainty of 17.4% [11]. The offset in the ellipsometry data of 0.480 nm was attributed to carbonaceous and water contaminations and, if that varied by just, say, 0.07 nm from sample to sample, the 0.089 nm scatter could be explained.

It is not the purpose here to detail or evaluate the results of the CCQM pilot study but to extract the main conclusions that help establish XPS as an accurate metrology tool. By comparison with the other XPS measurements using their local procedures for quantification, the average m and c val-

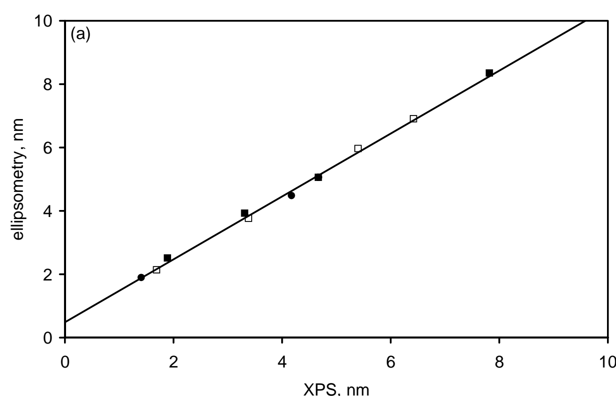

Fig. 4 Correlation plot of the ellipsometry data from NPL, with the NPL reference values determined by XPS using the reference geometry. The least-squares-fitted straight line gives the gradient m as a scaling constant and the intercept c as an offset value. The rms scatter of the results about the line gives a measure of the combined repeatabilities of the two methods. The European samples are shown for (100) (■) and (111) (□) substrates; the US samples are only for (100) (●) substrates. Note that these data are for samples soon after preparation and without removal from a dust-free environment between manufacture and ellipsometric measurement, after Seah *et al.* [11].

ues were 1.045 ± 0.145 and 0.172 ± 0.368 nm, respectively, where the uncertainties are standard uncertainties. Where laboratories also provided data using the reference geometry and the data were re-quantified using the NPL values for R_o and L, these m and c values improved dramatically to 1.001 ± 0.026 and -0.013 ± 0.110 nm, showing that XPS was a reliable analytical method. The uncertainties in these results were often dominated by counting statistic uncertainties where older monochromated instruments were used.

Analysis of all the data [11] led to m = 0.988 ± 0.016 if the data were unweighted or 0.986 ± 0.004 if they were weighted by inverse variances. This latter value implied that the value of L used should have been reduced by 1.4%.

The high quality of the respondee data in the CCQM pilot study indicated that a detailed evaluation of the measurement uncertainties could be rewarding.

5. Reducing the uncertainties in XPS

In evaluating the uncertainties for XPS, certain contributions have already been described. Additional contributions involve the counting statistics, the accuracy of the geometry, the spectrometer acceptance angle and the angle between the X-ray beam and the spectrometer input lens [17]. The latter contribution arises from the dipole asymmetry term, β, and is estimated to cause variation within a limit of ± 0.75% [11]. The input lens acceptance should not be small or forward focusing fine structure may be observed. Beyond a cone half-angle of 10°, results could bias by more than 0.5% and so a cone half-angle of 6° is recommended [17]. In terms of the counts, the sum of the Si 2p peaks should exceed 400000 for 0.5% precision and 100000 for 1% precision [17]. At NPL, we use the Mg Kα X-ray source, 20 eV pass energy, 0.1 eV energy step intervals, and a total dwell time per channel of 1 second. This generates 800000 counts for the Si 2p peak area. In terms of the uncertainty in the angle of emission θ, it is easy to see that 1° uncertainty leads to ~1% uncertainty in d.

Most surface analysis instruments have vacuum chambers where the port alignments are estimated to be valid to 1° but one needs knowledge of the relative setting of the sample tilt mechanism and of the spectrometer input lens to define any angular error. Added to these contributions is the effect of stray magnetic fields that may shift the electron optic axis of the input lens away from the mechanical axis. All these terms lead to a systematic bias in addition to the precision of setting the tilt. At NPL, our precision in setting the tilt angle had been around 1° and precisions better than this had been achieved by averaging many data.

In order to improve the accuracy of the geometrical setting, a laser pointer was used to indicate the sample tilt using a sample stub with an angle block with three attached mirrors set at appropriate angles that were accurately measured [18]. This angle block allowed the measurement of the orientation of the sample stub rather than the sample stage, so removing any errors associated with the seating of the stub on the stage. Using a sample cut with its surface accurately in the (100) plane, the zero of tilt could be established using the forward focusing pattern to ± 0.04°. This direction was slightly different from that for the geometric axis and different again from the previously used sample tilt setting value. With samples set accurately at their respective geometries, it was found that there was a shift of approximately 1.89° where the earlier data had been recorded at too high an emission angle, leading to results that were typically a factor of 1.025 too high in thickness. The new method led to a marked improvement in the repeatability of measurements, as shown in Fig 5. The two plotted lines are the predictions for 0.32° repeatability in the angular setting. This represents a factor of 3 improvement on the data shown in reference [17]. Note that the smaller emission angle for the (111) surfaces leads to a significantly better repeatability standard deviation of 0.27%.

From the revision to the results from the CCQM pilot study, using the above procedures, if R_o is taken as 0.9329 at the RG, then L is 2.996 ± 0.016 nm and 3.485 ± 0.019 nm for Mg and Al Kα X-rays, respectively. At 95% confidence, this would indicate that an uncertainty of 1.5% is possible, fitting the ITRS requirement of better than 4% at 3σ by nearly a factor of 2.

To verify the extent that this is achievable in practice, a CCQM key comparison is in progress and will report in 2006.

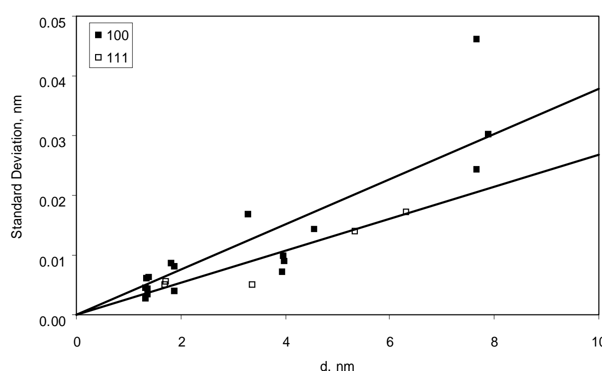

Fig 5 Standard deviations of repeated measurements for the (100) (■) and the (111) (□) samples.

6. Conclusions

XPS is a highly repeatable method for the analysis of the thicknesses of ultra-thin films in the range 1.5 - 8 nm at the surface. To achieve a standard uncertainty below 1%, it is important to be able to use peaks as close in energy as possible and peaks that characterise only the layer required and the substrate. If peaks other than those used here are chosen, such as that for O1s instead of the oxide Si 2p states, the analysis includes all other oxygen containing films such as adventitious contaminations. By using peaks close in energy, any effect of contaminants is avoided.

To achieve the required measurement accuracy, the total counts in the Si 2p peak should exceed 200000 counts and additionally, the total standard uncertainty in setting the angle of emission should be better than 0.7°. With an instrument over 20 years old this was surpassed using the Mg Kα X-ray source and by using a small mirror block on the sample stage with a cheap laser pointer.

XPS is linear and repeatable at the required level of accuracy in the system of SiO_2 on Si when using the NPL reference geometry but the key parameter, the attenuation length, may have uncertainties as high as 20% if the predictive equation TPP-2M [19] has to be used. A value of better than 1% uncertainty can only be obtained by determination of the attenuation length by using other methods such as ellipsometry, GIXRR or NR [11]. For these, if bulk values of parameters are to be used, the films to be analysed must be bulk-like. If this is not the case, the uncertainties may increase. Here, the thermal oxide is very close to bulk in its properties and so the issue is satisfied. An alternative calibration method, not studied here, but used by others [20] is the atomic force microscope. This looks promising, especially where the films can be grown over a wide range of thicknesses. The use of XPS with the relevant attenuation length determined by ellipsometry, GIXRR, NR and, maybe, other methods, thus provides a robust and highly accurate general method for measuring the thicknesses of ultra-thin films at surfaces.

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