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CCQM-K32 Key Comparison and P84 Pilot Study Amount of silicon oxide as a thickness of SiO_2 on Si

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ABSTRACT

CCQM-K32 and P84 were conducted following the pilot study P-38 to demonstrate and document the capability of interested National Metrology Institutes to measure the amount of silicon oxide on silicon wafers expressed as a thickness of SiO_2 for nominal thicknesses in the range 1.5 nm to 8 nm. "Amount of substance" may be expressed in many ways and here the measurand is the thickness of the silicon oxide layer on each of a total of 9 samples of nominal thicknesses in the range 1.5 to 8 nm on (100) and (111) Si substrates, expressed as the thickness of SiO_2. This report presents the results from K32 and P84. It includes the data received for the measured values and their associated uncertainties, at 95% confidence, for the 9 samples prior to the deadline for receipt of data. The materials are grown by thermal oxidation in very clean furnaces designed for high quality gate oxides on Si wafers in European and US facilities at the same time as those for the pilot study, P-38. Separate samples were provided to each institute in special containers limiting the carbonaceous contamination to below about 0.3 nm. The 9 samples included 5 samples of ultra-thin SiO_2 on (100) orientated wafers of Si and 4 samples of ultra-thin SiO_2 on (111) orientated wafers of Si.

The measurements from the 11 participating laboratories were conducted using ellipsometry, neutron reflectivity (NR), X-ray photoelectron spectroscopy (XPS) or X-ray reflectivity measurements (XRR), guided by the protocol developed in the pilot study P-38 and reproduced in the Appendix. The measurements are given in Tables 2 and 3. A very small correction is then made for the different samples that each laboratory received as in Table 4. Where appropriate, method offset values deduced from the pilot study P-38 are given in Table 5 leading to comparative data in Tables 6 and 7. Values for the Key Comparison Reference Values (KCRVs) and their associated uncertainties are made from the weighted means and the expanded weighted standard deviations of the means from Table 6. This is provided in Table 8. Graphical plots of equivalence from Tables 6 and 8 are provided in Figure 1 and equivalence statements are presented in Annex A. Additional XPS and XRR data from NMIJ for K32 were withdrawn from the KCRV evaluation and are given in Annex B.

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Approved on behalf of the Managing Director, NPL
by Dr Martyn Sené, Director, Quality of Life Division

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Table of Contents

1 Introduction **1**
2 CCQM-K32 and P84 ..... **1**
2.1 Objective 1
2.2 Participation 1
3 The test material **2**
3.1 Production 2
3.2 Initial characterisation of the test material 2
3.3 Sample distribution and deadline for reporting results 3
3.4 Instructions to the participants 4
3.5 The protocol 4
4 The participants' measurement procedures **4**
4.1 Methods, instrumentation and brief experimental details 4
5 Results **5**
6 Comparison of data **7**
7 Conclusions concerning the data analysis **14**
8 Equivalence statements **14**
9 Analysis of uncertainties **14**
9.1 XPS 15
9.2 XRR 18
9.3 NR 19
9.4 Ellipsometry 19
10 Conclusions and how far does the light shine? **21**
11 Acknowledgements **22**
References **22**
Annex A, Equivalence statements **23**
Annex B, NMIJ XPS and XRR Data **28**
Appendix, CCQM-K32 Protocol for measurements **31**

Tables & Figures

TABLES:

Table 2..........6

Table 3..........6

Table 4..........7

Table 5..........8

Table 6..........9

Table 7..........9

Table 8..........10

Table 9..........20

Table B.1..........28

Table B.2..........28

Table B.3..........29

FIGURES:

Figure 1..........13

1 Introduction

CCQM-K32 key comparison on measuring the amount of silicon oxide on Si expressed as a thickness of SiO_2 was proposed and discussed at the April 2004 CCQM Surface Analysis Working Group Meeting in Paris as a follow-up to the pilot study P-38, published in reference [1]. The aim of the study is to demonstrate and document the capability of interested National Metrology Institutes to measure silicon oxide thicknesses.

Ultra thin films are important in many different sectors of advanced industries ranging from microelectronics, memory devices and micro-electromechanical systems (MEMS) to sensors, bio-nanotechnology and X-ray mirrors. For efficiency, quality and yield reasons, these films need to be controlled and characterised. In some cases such as gate oxides, measurements are required at 1% accuracy. The ultra-thin film that is most thoroughly understood and characterised is that of thermal SiO_2 grown on (100) or (111) orientation pure Si wafers. Much work has been completed, in the past, on films 20 nm to 200 nm thick but, today, interest focuses in the 1.5 nm to 8 nm range. For these reasons and because high quality material was being grown in expert laboratories, the present intercomparisons focused on the thermal oxide of silicon in the range 1.5 nm to 8 nm thickness. Silicon oxides made by other routes may have different stoichiometries, densities, defect levels and other properties. The extent that this study directly illuminates their measurement depends on how closely their properties match those of the thermal oxide.

The pilot study P-38 [1] has already shown that the historical view of the hierarchy of the accuracies of relevant methods required revision and that some methods thought to be good turned out to be less good and vice versa. This resulted in a much improved understanding of the uncertainty contributions in most analytical methods and hence, in some cases, to their further development. It has also resulted in an improved understanding of the measurement methods themselves and hence to an improved infrastructure for the general measurement of ultra-thin films of this and of other compositions. Prior to these studies, the inter-method scatter range approached 100% in the sub-4 nm film thicknesses. In the pilot study P-38, offsets arising from surface contaminations of water and carbonaceous matter were identified in a range of methods and, when these were removed, this scatter reduced to around 5%. This was a major improvement. The present report provides the results from the key comparison, K32, and the pilot study, P84.

2 CCQM-K32 and P84

2.1 Objective

The measurand in this study is the thickness of the silicon oxide layer on each of a total of 9 samples of nominal thicknesses in the range 1.5 to 8 nm on (100) and (111) Si substrates, expressed as the thickness of SiO_2. The participants were free to choose their analytical method.

2.2 Participation

In April 2004, CCQM surface analysis working group (SAWG) members and other interested parties were informed about the organisation of the key comparison. Individual e-mails were

sent to those registering on 16 February 2005 and to all of the NMI representatives on 6 April 2005 prior to announcing it in the April 2005 sessions.

Finally, 9 institutes participated in CCQM-K32 and 4 in P84. In Germany, the two institutes participated in K32 in different thickness ranges. The order in Table 1 and on the front page is simply the order of receipt of results by the lead laboratory.

Table 1: Participants in K32 and P84.

No.	Institute/Organisation	Country	Contact Person	K or P
1	NPL	UK	Steve Spencer	K32
2	NRCCRM	China	Hai Wang	K32
3	NMISA (formerly CSIR-NML as shown in the Tables, text and Figs)	South Africa	Werner Jordaan	K32
4	BAM	Germany	Thomas Gross	K32
5	NIST	USA	Joseph Dura	K32
6	KRISS	Korea	Dae Won Moon	K32
7	NIMT	Thailand	Pian Totarong	K32
8	PTB	Germany	Michael Krumrey	K32
9	NIMJ	Japan	Isao Kojima	K32
10	EMPA	Switzerland	Roland Hauert	P84
11	BAM	Germany	Thomas Gross	P84
12	PTB	Germany	Michael Krumrey	P84
13	PSB	Singapore	Mo Zhiqiang	P84

3 The test material

3.1 Production

The material for K32 and P84 is from batches made with those for the pilot study P-38. Batches were made both in the US and in Europe on (100) and (111) Si substrates using furnaces especially designed for uniform ultra-thin thermal oxide growth in the 1.5 nm to 8 nm regime. Sufficient material was available that all participants received material not previously used for any measurements except for the ellipsometric mapping discussed in 3.2.

3.2 Initial characterisation of the test material

After production, the US material was provided in a sealed dust-free container to the European facility where all of the samples were mapped for the oxide thickness using a Philips PZ 2000 ellipsometer designed for production-line thickness determination. This instrument provided maps with a precision around 0.002 nm, allowing samples to be selected from regions that were homogeneous to within ±1%. An example of a map, in colour, is given in plate 1 of reference [2]. That particular sample shows a central region of 80 mm diameter that could have been used in these studies but other samples were more homogeneous and so were used instead. Analysis by XPS shows that these ellipsometry maps are accurate, as discussed below, for relative thicknesses in each wafer. Production technology has improved as a result of this mapping.

In order to ensure the best accuracy, the thickness of each sample provided to analysts was recorded for its position in each ellipsometry map. The 9 thicknesses chosen for this study were five of (100) Si, being of nominal thicknesses 1.5, 2, 3, 4, and 8 nm, together with four of (111) Si, being of nominal thicknesses 2, 3, 5 and 6 nm. The (100) Si wafers were cut into squares bounded by the (111) planes defining the [110] directions, whereas the (111) wafers were cut into triangles bounded by the same planes and directions [3].

After cutting, the samples were blown with an argon jet to remove cutting debris and then most of the carbonaceous contamination was removed by an overnight (16h) soak in high purity isopropyl alcohol (IPA), ultrasonic agitation in fresh IPA and blow drying with an argon jet. In this way, the thickness of the remaining carbonaceous contamination could be reduced from, typically, 0.64 nm [4] to a layer typically 0.12 nm thick [4]. Cleaning to remove this final layer requires more aggressive methods. UV with ozone achieves this but at the expense of affecting the oxide. This final carbonaceous layer is thought to be a catalytically reduced carbon layer with sp2 bonding. These carbonaceous thicknesses were measured by XPS with undefined uncertainties. Subsequent XPS measurements of storage in different containers showed that there was then an additional carbonaceous contamination thickness that increased approximately with the square root of time over the first 100 days and that polypropylene "Fluoroware" would typically keep the contamination below 0.25 nm for 3 months [4]. Fluoroware is commonly used for wafer containment. Samples were therefore supplied in these containers, only to be opened just prior to use.

In addition to the growth of the carbonaceous contamination, repeat XPS measurements of the oxide thicknesses have been made for one set of the samples stored in the Fluoroware containers after 6 months. The average increase in the oxide thickness over the six months, as measured by XPS, is 0.001 ± 0.059 nm. The samples are thus assumed to be stable for the period of the measurements reported here. The samples were despatched from May 2005.

3.3 Sample distribution and deadline for reporting results

Discussions were held with participants concerning their requirements for sample numbers and sizes. Standard sets comprised the five (100) samples, cut as squares 10 mm by 10 mm, whereas the four (111) samples were cut as equilateral triangles of side 15 mm. These were couriered to laboratories on 18 May 2005. A few participants requested other geometries or much larger samples. These larger samples were for methods where beams requiring a large area were to be used. These samples were uniform to 1% over the analytical area but may have diverged from this in regions at their edges where they were to be covered by a sample mount during analysis or where this rim was not for analysis. These participants, and those who confirmed their sample size later, received samples that were couriered in the period up to 2 June 2005. Approximately 100 samples were prepared.

The deadline, after discussion with participants and in the April 2005 SAWG meeting, was set at 18 September 2005. At the beginning of September 2005, after several requests and with the agreement of participants, this was extended to 18 October 2005. None of the data were accessed until after this date. The draft A report was sent to those listed on page 1 and to the CCQM SAWG Chairman on 5 December 2005.

3.4 Instructions to the participants

The couriered package contained

- a 1 page covering letter with the specific serial codes for each sample,
- a protocol of 7 pages (see Appendix),
- the samples, each in separate Fluoroware containers (max 9).

3.5 The protocol

The protocol, shown in the Appendix, contained

- a statement of the objectives,
- the timetable,
- details of the material, sample handling and any necessary cleaning,
- details of issues to report including details of the uncertainty calculation for 95% confidence,
- suggestions for the model of SiO_2 on Si with approximately a monolayer of intermediate interfacial oxides and a surface layer of adsorbed hydrocarbons, organics etc as well as water,
- an example table for the reported thicknesses and uncertainties (a mandatory pro-forma table was considered inappropriate at the April 2005 CCQM SAWG meeting).

4 The participants' measurement procedures

All participants have submitted results with uncertainties except PSB who were in the pilot study, P84. PSB provided repeatability data. They all stated a functional relationship and all except PSB described various uncertainty contributions of the uncertainty budget. Some also submitted a complete and detailed analysis report. In the following paragraphs, the methods are summarised.

4.1 Methods, instrumentation and brief experimental details

For the key comparison, K32:

1) NPL used X-ray photoelectron spectroscopy (XPS) with a VG Scientific ESCALAB II with a 210 analyser involving Mg Kα X-rays at the magic angle and the NPL reference geometry with R_o = 0.9329 and L = 2.996 nm, as cited by M P Seah and S J Spencer [5]. XPS is always conducted in ultra-high vacuum.

2) NRCCRM used XPS with a VG Scientific ESCALAB 220i-XL involving Mg Kα X-rays at the magic angle and the NPL reference geometry with R_o = 0.9329 and L = 2.964 nm, as cited by M P Seah *et al* in the earlier report [1].

3) CSIR-NML used XPS with a Physical Electronics Quantum 2000 involving Al Kα X-rays and the NPL reference geometry with R_o = 0.933, as cited by M P Seah *et al* [1], and L = 3.485 nm, as cited by M P Seah and S J Spencer [5].

4) BAM used XPS with a Kratos Axis Ultra DLD involving Mg Kα X-rays and the NPL reference geometry with R_o = 0.9329 and L = 2.996 nm, as cited by M P Seah and S J Spencer [5].

5) NIST used neutron reflectometry (NR) in vacuum with cold neutrons of wavelength 0.475 nm, as discussed in M P Seah *et al* [1] and more generally by Dura *et al* [6].

6) KRISS used XPS incorporating a Scienta SES-100 electron spectrometer with a SPECS XR-50 Mg K α X-ray source and the NPL reference geometry with R_o = 0.933, as cited by M P Seah *et al* [1] and L = 2.996 nm, as cited by M P Seah and S J Spencer [5].

7) NIMT and the Thai Microelectronics Center (TMEC) used ellipsometry in ambient air with a dual wavelength (HeNe laser for 633 nm beam and 780 nm laser diode) focused beam FE III Focus Ellipsometer (Rudolph Technologies Inc., New Jersey, USA) for simultaneous multi-angle measurements with in-built data processing and calibration.

8) PTB used X-ray reflectometry (XRR) at BESSY II in vacuum at a photon energy of 1841 eV, combined with new X-ray fluorescence (XRF) measurements at a photon energy of 480 eV.

9) NMIJ used XPS for the three thinnest samples ≤ 2 nm and grazing incidence XRR (GIXRR) for those six that were thicker than 2 nm. The XPS was conducted with a VG Scientific ESCALAB 220i-XL involving Al Kα X-rays at the magic angle and with emission normal to the surface. The value of R_o was obtained from a plot of I_{SiO2} versus I_{Si} and L from the gradient of a plot of $\ln(1+R/R_o)$ versus d_{GIXRR}. These gave R_o = 0.732 ± 0.012 and L = 3.626 ± 0.023 nm. The GIXRR measurements were made using a Rigaku ATX-G2 rotating anode Cu Kα source with a channel cut Ge(220) monochromator, as discussed by Kojima and Li [7,8].

For the pilot study, P84:

10) EMPA used XPS with a Physical Electronics Quantum 2000 involving Al Kα X-rays and the NPL reference geometry with R_o = 0.933 and L = 3.448 nm, as cited by M P Seah *et al* [1].

11) BAM used XPS, as noted at 4) for the thicker films.

12) PTB used XRR as noted at 8) for the thinner films

13) PSB corp. used XPS with an ULVAC-PHI Quantera SXM involving Al Kα X-rays at an emission angle of 45° with R_o = 0.896 determined experimentally and L = 3.448 nm.

5 Results

The values of the thicknesses and their associated uncertainties at a 95% level of confidence are given in Table 2 for K32 and Table 3 for P84.

Table 2: CCQM-K32 participants' results for the equivalent thicknesses of SiO_2 and their associated uncertainties; *d* = thickness, *U* = uncertainty for a 95% confidence interval. (NB: These are for individual samples and for comparison need correcting to a reference sample)

Participant	(100) material										(111) material							
	"1.5 nm"		"2 nm"		"3 nm"		"4 nm"		"8 nm"		"2 nm"		"3 nm"		"5 nm"		"6 nm"	
	d nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm
1, NPL	1.362	0.033	1.783	0.037	3.218	0.056	3.954	0.066	7.607	0.121	1.692	0.034	3.280	0.050	5.265	0.074	6.191	0.086
2, NRCCRM	1.450	0.068	1.892	0.088	3.281	0.158	4.013	0.194	7.159	0.416	1.759	0.082	3.323	0.154	5.249	0.274	6.083	0.426
3, CSIR-NML	1.34	0.10	1.70	0.12	3.16	0.18	3.88	0.22	7.60	0.31	1.63	0.13	3.20	0.18	5.19	0.23	6.15	0.25
4, BAM	1.48	0.05	1.91	0.07							1.69	0.06						
5, NIST	1.752	0.038					4.169	0.023			1.982	0.051			5.595	0.030		
6, KRISS	1.360	0.046	1.821	0.061	3.289	0.108	4.102	0.158	7.819	0.323								
7, NIMT	1.967	0.53030	2.322	0.52768	3.831	0.53044	4.576	0.53052	8.386	0.53674	2.314	0.53016	3.915	0.53304	5.921	0.54030	6.961	0.53812
8, PTB					3.38	0.12	4.28	0.12	7.72	0.12			3.54	0.12	5.57	0.12	6.41	0.12
9, NMIJ	1.28	0.62	1.83	0.62	3.57	0.17	4.53	0.11	7.93	0.09	1.67	0.62	3.89	0.08	5.91	0.26	6.83	0.07

Table 3: CCQM-P84 participants' results for the equivalent thicknesses of SiO_2 and their associated uncertainties; *d* = thickness, *U* = uncertainty for a 95% confidence interval. (NB: These are for individual samples and for comparison need correcting to a reference sample)

Participant	(100) material										(111) material							
	"1.5 nm"		"2 nm"		"3 nm"		"4 nm"		"8 nm"		"2 nm"		"3 nm"		"5 nm"		"6 nm"	
	d nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm
10, EMPA[a]	1.250	0.245	1.725	0.325	3.190	0.550	4.020	0.670	7.780	1.175	1.575	0.305	3.205	0.560	5.305	0.855	6.350	1.000
11, BAM					3.35	0.12	4.24	0.16	7.43	0.27			3.34	0.12	5.19	0.19	6.16	0.23
12, PTB	1.71	0.12	2.06	0.12							2.05	0.12						
13, PSB[b]	1.39		1.83		3.29		4.00		7.57		1.76		3.42		5.37		6.32	

[a] Two different points have been measured on each sample. The table shows the mean and the average uncertainty.
[b] No uncertainties were provided.

6 Comparison of data

For the comparison of data, two adjustments are required. Firstly, each of the individual samples has its own individual thickness, as noted above, characterised by the ellipsometry map measurements just after manufacture. For comparison of the laboratories with each other, the differences in the thicknesses of each sample from a reference sample need to be subtracted and the additional uncertainty associated with this adjustment added. These differences have been measured and are given in Table 4. It is clear from this table that the average of the total ranges for these samples from their median is less than 0.8% of the absolute thickness. This small value was obtained by careful selection of the material available. These differences, with a mean magnitude of 0.02 nm, have an associated uncertainty at 95% confidence of 0.06 nm. This uncertainty arises from comparisons of randomly selected samples and includes the two separate ellipsometric measurements and the two XPS measurements required to confirm each thickness difference. This uncertainty is probably an overestimate but has been added in quadrature to the values given in Tables 2 and 3 before plotting in Figure 1 showing the degrees of equivalence.

Table 4: Individual sample thickness, nm, minus the thickness of a reference sample, nm, for each nominal thickness, as determined in the original ellipsometry maps.

Participant	100					111			
	1.5nm	2nm	3nm	4nm	8nm	2nm	3nm	5nm	6nm
NPL	-0.019	-0.026	0.000	0.012	-0.063	-0.011	0.000	0.000	0.000
NRCCRM	0.000	0.000	0.000	0.000	-0.108	-0.011	0.018	-0.030	0.000
CSIR-NML	-0.011	0.000	0.015	0.012	-0.090	-0.011	0.000	0.000	0.000
BAM	0.000	-0.013	0.000	0.000	-0.108	0.000	0.018	-0.030	0.034
NIST	-0.015			0.000		-0.067		-0.043	
KRISS	-0.008	0.000	-0.003	0.023	0.000				
NIMT	-0.015	0.000	-0.003	0.023	-0.018	0.000	0.000	-0.061	0.000
PTB	-0.008	-0.013	-0.023	0.000	-0.094	-0.067	0.030	-0.030	0.000
NMIJ	-0.004	-0.026	-0.003	-0.006	-0.135	0.011	0.012	-0.030	0.034
EMPA	-0.011	0.000	-0.023	0.012	-0.090	0.011	0.000	-0.030	0.000
PSB	-0.004	-0.026	0.000	0.012	0.090	0.000	0.000	0.000	0.034

Secondly, corrections need to be applied for the effects of surface contaminations currently thought to be the source of the different offsets seen in thicknesses measured by the different methods. Discussions with colleagues at the Fritz Haber Institute studying interactions at SiO_2 surfaces indicate that adsorbing hydrocarbons catalytically dehydrogenate at a clean SiO_2 surface. This continues until the active sites are all covered with a layer of "coke". Thus, the adventitious contamination is likely to include a thin carbon layer of the order of a fraction of a monolayer of carbon (0.2 nm), covered with a thin hydrocarbon layer whose thickness grows with the square root of time. Added to this layer will be both chemisorbed and physisorbed water and the extent of that water will, for measurements in air, depend on the relative humidity [9-11] and, maybe, the extent of hydrocarbon uptake. Measurements [9-11] indicate that the physisorbed water thickness could be between 0.05 nm and 0.3 nm. Azuma *et al* [12] show, by XRR, by fitting with a 2-layer model instead of a 1-layer model, that the full extent of the water layer in air is 0.55 to 0.67 nm for thermal oxides of similar thicknesses to those measured here. Furthermore, they show by thermal desorption

spectrometry, that the water requires 800 ºC for removal of water in the α, β_1 and β_2 chemisorption states.

Chemical shift data for the C 1s peak from XPS are consistent with the carbon-based part of this model but hydrogen is not directly observable. Very recent data from BAM confirm this dehydrogenated layer with observation by near edge X-ray Absorption Fine Structure spectroscopy (NEXAFS) which show a clear, narrow and intense C 1s → π*(C=C) resonance at the appropriate energy in the spectrum.

NR and XRR simulations show that the above contamination is consistent with the discrepancy, identified in the pilot study P-38, between NR and XPS and also XRR and XPS. The most plausible explanation available for NR and synchrotron XRR data is that a combination of carbon, hydrocarbons and water creates a contamination layer that has a scattering length density (SLD) close enough to SiO_2 to be indistinguishable from SiO_2 and that the pilot study P-38 offsets [1,13] measure this effect and permit them to be subtracted. These offsets are given in Table 5. These have been determined from the data given in the pilot study P-38 [1,13] but instead of fitting a line and establishing a gradient, *m*, and offset, *c*, the absolute difference is calculated directly from the same data for each thickness, using the calibrated XPS attenuation length. The offsets for NIMT are established from the average offset between XPS and ellipsometry results for those responding to the pilot study P-38, adjusted for the reduction in contamination that arises from the use, in NIMT, of a hot stage.

Table 5: Offsets determined from the data for the pilot study, P-38.

Institute	Offset, nm	*k*, (No of results)	*k* times the standard deviation, nm
NIMT (ellipsometry)	0.78	2.447 (7)	0.39
PTB (XRR)	0.49	4.303 (3)	0.29
NIST (NR)	0.22	3.182 (4)	0.26

The values that may be compared are thus the Table 1 values minus the Table 4 and Table 5 values with those 95% confidence uncertainties combined in quadrature. Note that the uncertainty of 0.06 nm for the sample-to-sample uncertainty propagates through to the KCRV uncertainty. These results are shown in Tables 6 and 7 except for the XPS and XRR data from NMIJ which were subsequently withdrawn from the KCRV evaluation and are shown in Annex B. The KCRV values and their associated uncertainties are now calculated from the weighted averages from Table 6, as shown in Table 8. The uncertainties use *k* values, from Student's tables, that are in excess of 2 to allow for the relevant degrees of freedom.

Table 6: CCQM-K32 participants' results for the equivalent thicknesses of SiO_2 and their associated uncertainties; *d* = thickness, *U* = uncertainty for a 95% confidence interval. (NB: These are for individual samples and for comparison have been corrected to a reference sample)

Participant	(100) material										(111) material							
	"1.5 nm"		"2 nm"		"3 nm"		"4 nm"		"8 nm"		"2 nm"		"3 nm"		"5 nm"		"6 nm"	
	d nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm
1, NPL	1.381	0.068	1.809	0.070	3.218	0.082	3.942	0.089	7.670	0.135	1.703	0.069	3.280	0.078	5.265	0.095	6.191	0.105
2, NRCCRM	1.450	0.091	1.892	0.107	3.281	0.169	4.013	0.203	7.267	0.420	1.770	0.102	3.305	0.165	5.279	0.280	6.083	0.430
3, CSIR-NML	1.351	0.117	1.700	0.134	3.145	0.190	3.868	0.228	7.690	0.316	1.641	0.143	3.200	0.190	5.190	0.238	6.150	0.257
4, BAM	1.480	0.078	1.923	0.092							1.690	0.085						
5, NIST	1.547	0.271					3.949	0.270			1.829	0.274			5.418	0.270		
6, KRISS	1.368	0.076	1.821	0.086	3.292	0.124	4.079	0.169	7.819	0.329								
7, NIMT	1.197	0.663	1.537	0.661	3.049	0.663	3.768	0.664	7.619	0.669	1.529	0.663	3.130	0.666	5.197	0.671	6.176	0.670
8, PTB					3.123	0.318	4.000	0.318	7.534	0.318			3.230	0.318	5.320	0.318	6.130	0.318

Table 7: CCQM-P84 participants' results for the equivalent thicknesses of SiO_2 and their associated uncertainties; *d* = thickness, *U* = uncertainty for a 95% confidence interval. (NB: These are for individual samples and for comparison have been corrected to a reference sample)

Participant	(100) material										(111) material							
	"1.5 nm"		"2 nm"		"3 nm"		"4 nm"		"8 nm"		"2 nm"		"3 nm"		"5 nm"		"6 nm"	
	d nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm
10, EMPA[a]	1.261	0.252	1.725	0.330	3.213	0.553	4.008	0.673	7.870	1.177	1.564	0.311	3.205	0.563	5.335	0.857	6.350	1.002
11, BAM					3.350	0.134	4.240	0.171	7.538	0.277			3.322	0.134	5.220	0.199	6.126	0.238
12, PTB	1.438	0.318	1.793	0.318							1.837	0.318						
13, PSB[b]	1.394		1.856		3.290		3.988		7.480		1.760		3.420		5.370		6.286	

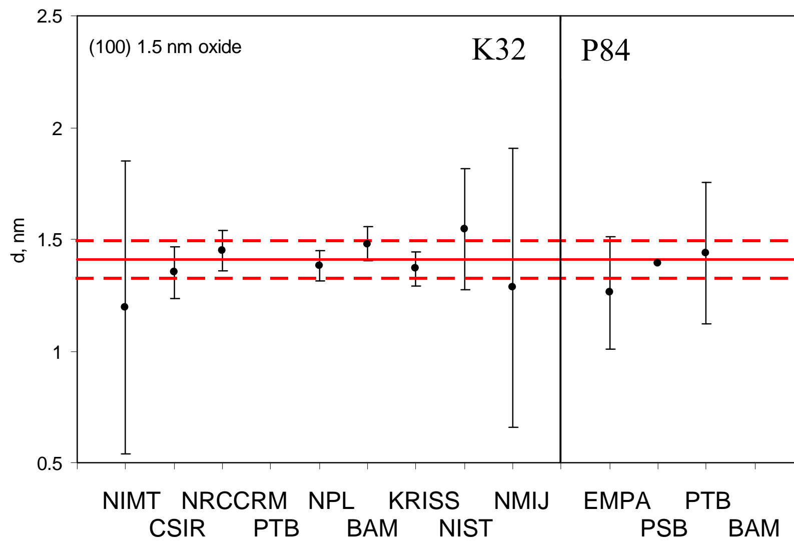
[a] Two different points have been measured on each sample.

[b] No uncertainties were provided.

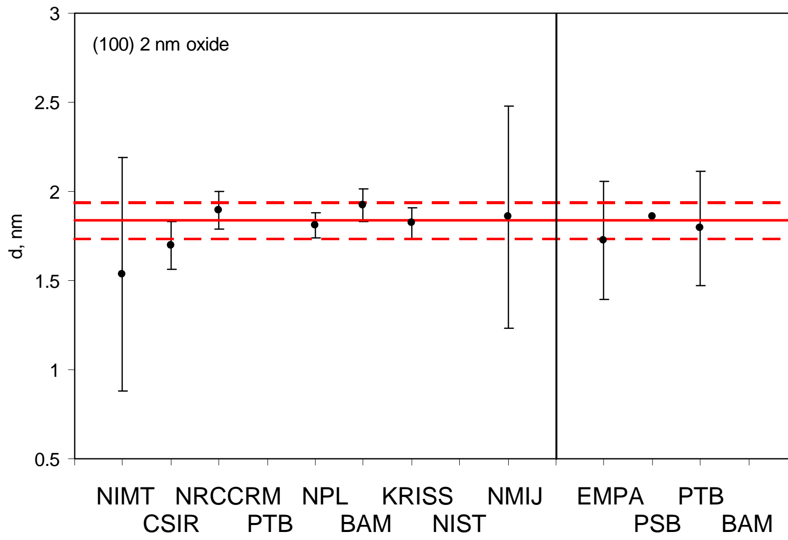
Table 8: Key Comparison Reference Values (KCRVs) from the weighted means with the uncertainties for 95% confidence intervals from *k* times the standard deviations.

Substrate orientation	100					111			
Nominal thickness, nm	1.5	2	3	4	8	2	3	5	6
Weighted mean, d_R, nm	1.41	1.84	3.23	3.97	7.65	1.71	3.27	5.27	6.18
k value	2.45	2.57	2.57	2.45	2.57	2.57	2.78	2.57	2.78
Uncertainty at 95% confidence, U_R, nm	0.09	0.10	0.15	0.16	0.27	0.11	0.18	0.20	0.25

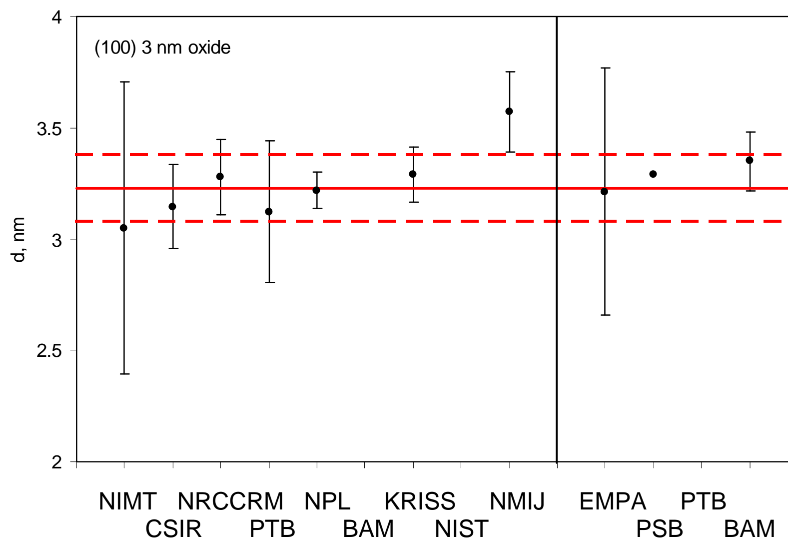
In the plots that follow, the first 9 values, reading from the left are for the key comparison laboratories. The laboratories are identified along the abscissa. The laboratory order in the key comparison set follows a convention that starts with the laboratory with the overall lowest average value and finishes with that reporting the highest overall average value. This is slightly different from the convention in which the order is set differently for each sample. Following the ten key comparison laboratories is a space where there is a vertical line dividing the two boxes at the value point "10", and then the four laboratories in the pilot study P84 are shown. Thus, in the Figure 1 (a), there is no value at "14" since the BAM value is in the key comparison, whereas for PTB at "13" there is a value but not at "4". In other plots, for the thicker materials, the roles of BAM and PTB reverse.



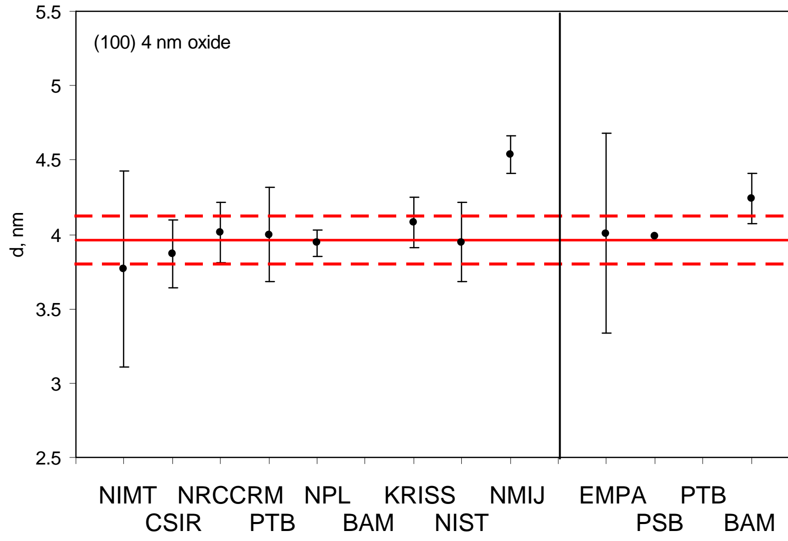
(a)



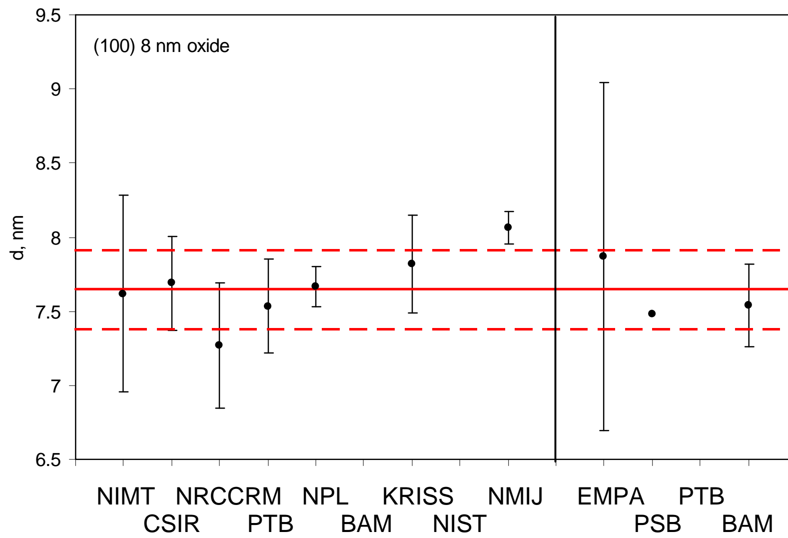
(b)



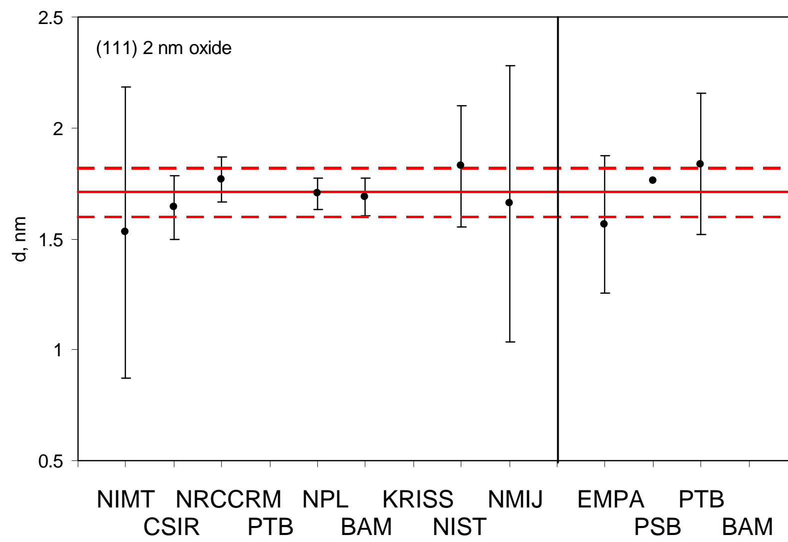
(c)



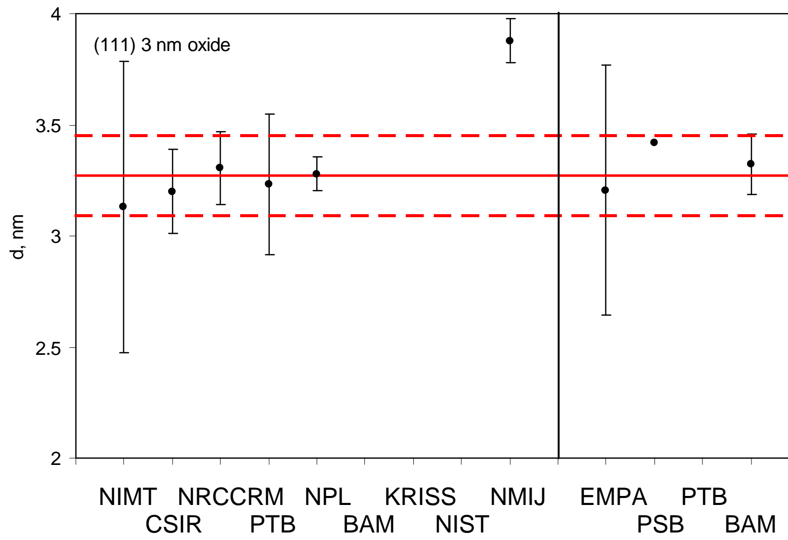
(d)



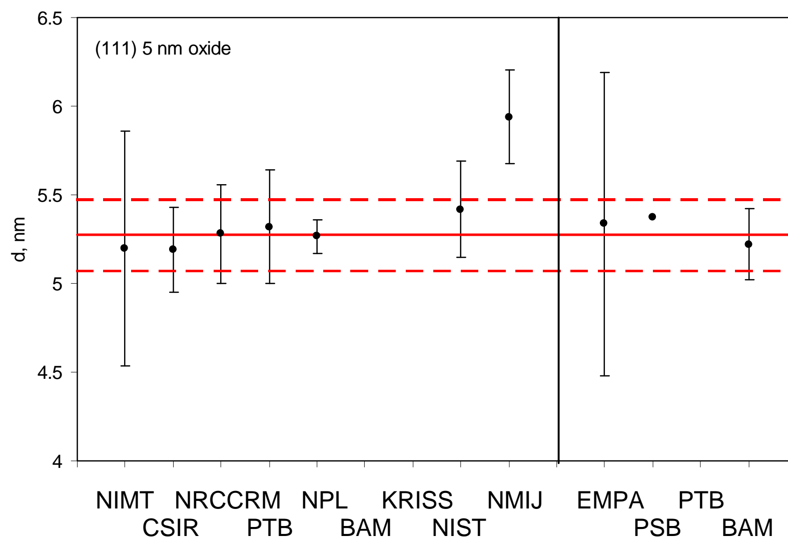
(e)



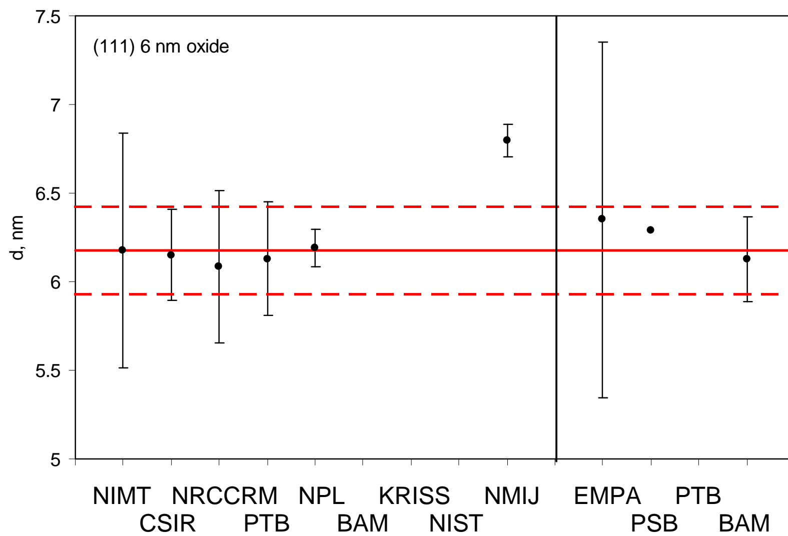
(f)



(g)



(h)



(i)

Figure 1 – K32 (to the left, from Table 6) and P84 (to the right from Table 7) thicknesses and their uncertainties at a confidence level of 95%. These data are corrected to a reference wafer with the sample to sample uncertainty added for intercomparison for the thicknesses of the (100) samples; (a) 1.5 nm, (b) 2 nm, (c) 3 nm, (d) 4 nm, (e) 8 nm; and (111) samples, (f) 2 nm, (g) 3 nm, (h) 5 nm, and (i) 6 nm. The solid and dashed red lines shows the KCRV and the 95% confidence intervals from Table 8, respectively.

7 Conclusions concerning the data analysis

From the reported data, the Table 8 data provide the KCRVs for the reference samples, and this may be used together with Table 4 to convert these values directly to the individual samples used by each participating laboratory.

8 Equivalence statements

The equivalence statements are calculated according to the BIPM guidelines. The degree of equivalence (and its uncertainty) between a NMI result and the KCRV is calculated according to the following equations:

$$D_i = d_i - d_{\mathrm{R}} \quad (1)$$

$$U_i^2 = U_{di}^2 + U_{\mathrm{R}}^2 \quad (2)$$

where D_i is the degree of equivalence between the NMI result given in Table 6, d_i, and the KCRV, d_{R}, and U_i is the expanded uncertainty (95% confidence) of the D_i calculated from the expanded uncertainty of the NMI result U_{di} and the expanded uncertainty of the KCRV, U_{R}. The uncertainty of the NMI result is given by combining the uncertainties in Tables 2 and 5. That given in Table 6 is not used since it includes the sample-to-sample uncertainty which is included also in U_{R}. The equivalence statements of CCQM-K32 are presented in Annex A. The matrix representing the degree of equivalence between two NMI results is no longer part of a final key-comparison report. The degree of equivalence (and its uncertainty) between two NMI results is calculated on request only, according to the following equations:

$$U_{ij}^2 = U_i^2 + U_j^2 \quad (3)$$

$$D_{ij} = d_i - d_j \quad (4)$$

where D_{ij} is the degree of equivalence between the NMI results d_i and d_j and U_{ij} is the expanded uncertainty of the D_{ij} calculated by the combined expanded uncertainties of the NMI results U_i and U_j.

9 Analysis of uncertainties

In order to calculate the weighted average for the KCRV, it is important that the stated uncertainties include all major contributions with appropriate estimates. To analyse the uncertainties reported by each laboratory in detail, the measurement methods need a brief description. Below, we discuss the measurement uncertainty contributions in each method used in the key comparison. The data for the associated pilot study P84 are included in the plots for information but are not included in any of the calculations or discussions of the uncertainties.

9.1 XPS

XPS measurements were conducted in the key comparison by NPL, NRCCRM, CSIR-NML, BAM, and KRISS. The basic method uses the intensities from the Si 2p peak for the SiO_2 and Si states, I_{SiO_2} and I_{Si}, respectively. If unmonochromated spectra are obtained, first the X-ray satellites are removed and then, in some cases to simplify the spectra, the spin-orbit splitting of 50% intensity at 0.60 eV higher binding energy can also removed by deconvolution. Where a monochromator is used, the satellite subtraction step is omitted. From these data, an equation often used to calculate the SiO_2 thickness, d, is

$$d = L\cos\theta \ln\left[1 + \left(I_{SiO_2} / R_o I_{Si}\right)\right] \tag{5}$$

where L is the attenuation length for the electrons measured in the SiO_2 overlayer, and R_o is the ratio of the intensities for bulk SiO_2 and bulk Si. This is known as the two peak method. In a slightly more accurate formulation, the intensities of the interfacial oxides Si_2O_3, SiO and Si_2O are also measured leading to a more complex set of equations. Equation (5) is then replaced by the following equations [1]:

$$d_{SiO_2} = L_{SiO_2} \cos\theta \ \ln\left[1 + \frac{\left(\dfrac{I_{SiO_2}}{R_{SiO_2}}\right)}{\left(\dfrac{I_{Si_2O_3}}{R_{Si_2O_3}} + \dfrac{I_{SiO}}{R_{SiO}} + \dfrac{I_{Si_2O}}{R_{Si_2O}} + I_{Si}\right)}\right] \tag{6}$$

$$d_{Si_2O_3} = L_{Si_2O_3} \cos\theta \ \ln\left[1 + \left(\frac{I_{Si_2O_3}}{R_{Si_2O_3}\ I_{Si}}\right)\right] \tag{7}$$

$$d_{SiO} = L_{SiO} \cos\theta \ \ln\left[1 + \left(\frac{I_{SiO}}{R_{SiO}\ I_{Si}}\right)\right] \tag{8}$$

and

$$d_{Si_2O} = L_{Si_2O} \cos\theta \ \ln\left[1 + \left(\frac{I_{Si_2O}}{R_{Si_2O}\ I_{Si}}\right)\right] \tag{9}$$

These thicknesses are then summed to give the effective SiO_2 thickness using the relation

$$d = d_{SiO_2} + 0.75\, d_{Si_2O_3} + 0.5\, d_{SiO} + 0.25\, d_{Si_2O} \tag{10}$$

Equation (10) apportions the thicknesses according to the oxygen content. The values of the $L_{Si_2O_x}$ and $R_{Si_2O_x}$ for x = 1 to 3 are interpolated linearly between the values for SiO_2 and Si [1,14]. In the pilot study P-38, it was noted that the three interfacial oxides contributed a thickness of 0.128 ± 0.008 nm, close to the estimated 0.124 nm for an ideal interface [1]. The use of the simpler Eq (5) instead of Eqs (6) to (10) does not simply give a difference of 0.128

nm since the fitting procedure for 2 peaks leads to a slightly higher value of I_{SiO_2} than that obtained where 5 peaks are used. The ratio of the thickness obtained using Eq (5) to that obtained using Eqs (6) to (10) with L_{SiO_2} and R_{SiO_2} unchanged rises from 1.003 at 1.5 nm thickness to 1.013 at 8 nm thickness [14], thus generating a difference significantly smaller than the 0.128 nm above.

In terms of the uncertainties for 95% confidence, the relevant relation is [14]

$$U^2 = U_E^2 + U_n^2 + U_\theta^2 + U_A^2 + U_P^2 + U_F^2 + U_L^2 \quad (11)$$

where U_n, U_θ, and U_A are terms for the laboratory's measurement statistics from the spectrometer signal, the angle setting and the analyser electron optics. The terms U_P and U_F are for the use of different numbers of peaks in the fitting of the data (as noted above) and the use of different peak shape algorithms. U_E is a term for the validity of the model of Eq (5) or Eqs (6) to (10) and U_L is the uncertainty in the attenuation length. The value of U_n may depend on the individual analysis and U_θ may be different for the (100) and (111) samples. U_n and U_θ have random, type A, contributions whereas the other terms largely involve type B contributions.

For analysis conducted using the reference geometry established by NPL [3], U_E is less than 0.025 nm [14,15], U_A is negligible for an analyser cone entrance semi-angle < 6° [16], U_P and U_F are negligible for fitting 5 peaks using valid software [16], and, if R_o is taken as 0.9329, then U_L, determined in the pilot study P-38 [13], is 0.0107d at an expansion of $k = 2$ for L taken as 2.996 nm or 3.485 nm for Mg or Al Kα X-rays, respectively. The uncertainty in R_o is accommodated in this expression. The remaining terms depend on the statistical quality of the data recorded.

At NPL, the above procedure was used for Mg Kα X-rays with the magic angle geometry. In addition, repeated analyses of 22 different (100) and (111) samples showed that the random components of U_n and U_θ gave contributions of 0.00769d and 0.00508d for (100) and (111) samples, respectively, with these values dominated by U_θ. The difference for (100) and (111) surfaces is expected from the 0.35° estimated precision of setting the respective values of θ. In addition to this is the accuracy of setting θ and the standard uncertainty for this was shown earlier [5] to be significantly less than the value of 0.35° used for this comparison. This value was expanded to 0.7° at $k = 2$. Use of these uncertainties leads directly to the values in Table 2. An issue that also needs discussion is the zero origin of the relation for d. For clean Si, d should be zero but this will not be observed with zero uncertainty as a result of statistical noise in the background under the peak. That U_E is 0.025 nm is confirmed for $d > 0.2$ nm in reference [14] and for the range down to 0.022 nm in reference [15].

At NRCCRM, the same experimental and data reduction procedure, X-rays, reference geometry and value for R_o were used, however, L has been taken as 2.964 nm [1] instead of the later value of 2.996 nm [5] and the peak fitting was conducted using 6 peaks without spin-orbit subtraction instead of 5 peaks after spin-orbit subtraction. The parameters U_F, U_P and U_A were estimated to be in the range 0.2 to 1.3% for the 9 samples. The random parts of U_n and U_θ were estimated from 6 repeat measurements with the mean being reported. The samples were repositioned each time. The standard deviations of these 6 measurements, in

the range 0.49% to 0.97%, were used for the unexpanded part of U_n and U_θ. This is a valid expression for a typical measurement which is how some participants view a key comparison. Another valid approach is to use the standard deviation of the mean which would reduce this contribution by a factor of $\sqrt{N}$, where $N = 6$. This is valid for understanding the uncertainty of the final result. Dominating all these contributions is an estimated standard uncertainty of 2% for the absolute value of the emission angle θ. The final standard uncertainties are all in the range 2.3% to 2.9%. These values are all expanded using $k = 2$ for listing in Table 2. The final uncertainty estimates agree with these estimates. If the later value of L is used, the reported values would all scale up by a factor of 1.011 – a factor well within the stated uncertainties.

At CSIR-NML, the same general procedure is applied except that now the Al Kα X-rays are obtained from a monochromator so that the higher value of L_{SiO_2} of 3.485 nm is used. The geometry is again the NPL reference geometry but this time the spin-orbit splitting is not subtracted but instead 6 peaks are fitted, 2 for the Si 2p elemental peak and one each for the remaining oxide states. Analysis shows that the likely error for this procedure is typically a standard uncertainty around 0.25%. Instead of using Eqs (6) to (10), a simpler equation:

$$d = L_{SiO_2} \cos\theta \ln\left[1 + \frac{I_{SiO_2} + 0.75 I_{Si_2O_3} + 0.5 I_{SiO} + 0.25 I_{Si_2O}}{R_o (I_{Si} + 0.75 I_{Si_2O} + 0.5 I_{SiO} + 0.25 I_{Si_2O_3})}\right] \quad (12)$$

is applied. This equation gives a result within a standard uncertainty of 0.6% of Eqs (6) to (10) [13]. The uncertainties are evaluated according to a version of Eq (11). U_E is taken as 0.025 nm, the random parts of U_n and U_θ are deduced from 3 measurements for each oxide thickness. Here the uncertainty is taken as k times the standard deviation of the mean with $k = 2$. The type B part of U_θ is estimated from a contribution of 2° with a rectangular distribution. Contributions of 5% have also been added for the statistical uncertainty of the low count levels of the main peaks I_{SiO_2} and I_{Si} in this monochromated instrument, 1% for the layer thickness homogeneity and 0.023 for the uncertainty in R_o, all from rectangular distributions. These give expanded values by first dividing by 1.73 (for the rectangular distribution) and then multiplying by 2. The added statistical uncertainty in the intensities is already reflected roughly in the standard deviation of the means of the 3 measurements. The layer thickness homogeneity is an uncertainty that is separately added, as discussed in the text relating to Table 4, and the uncertainty in R_o is already subsumed into that for L. The final uncertainty estimates thus partially include some aspects twice and thus include a margin of safety.

At BAM, the same experimental procedure, X-rays, reference geometry and values for L and R_o were used as in NPL. The input lens was stopped down to a semi-angle of 6° and 7 measurements were made on each sample. The calculational procedure used Eqs (6) to (10) but with 6 peaks after satellite subtraction. The spin-orbit splitting was not deconvolved but, instead, the elemental Si peak was represented by 2 peaks, as at CSIR-NML. The uncertainties from Eq (7) are taken with U_E, U_A, U_P and U_F as zero, U_L as 1.068%, U_n from the 7 measurements with 1.0% contribution to the major two intensities and a total of 2° and 0.8% added linearly for the geometry and forward focussing in U_θ, all at $k = 2$. This was all combined to give a total of 3.68% at $k = 2$, evaluated for the 1.5 nm (100) sample. This value was then applied to all samples. For the key comparison, this is valid since the 3 samples analysed were all of similar thicknesses.

At KRISS, the same experimental and data reduction procedure, X-rays, reference geometry and values for L and R_o were used as in NPL but only the (100) samples were analysed. Great care was taken to set the angles accurately with a laser system as described in reference [5]. Analyses were made with the 5-peak procedure with spin-orbit splitting on all peaks. Three measurements were made on each sample with repositioning. The uncertainty estimate is made from Eq (11) with U_E, U_A, U_P and U_F as zero, and with U_L as 1.08%, U_n, from the standard deviation of the means for the 3 measurements, is typically 2%. The expanded uncertainty of 2.4° for the angle setting gives U_θ = 2.84%. These values are all at k = 2 and give the total expanded Type B uncertainty of 3.04% whereas the type A uncertainty ranges from 1.22% to 2.79%. These give the uncertainties listed in Table 2.

9.2 XRR

In XRR, the defining equation for the interference relation is given by

$$n\lambda = 2d\sin\theta \tag{13}$$

where λ is the X-ray wavelength, n is the order of the interference and θ is the angle of incidence of the X-rays from the sample surface. In Eq (13), the terms are for parameters inside the layer. For parameters outside the layer, a small allowance for the refractive index of the layer needs to be included. For a single film, as θ is scanned, characteristic minima are observed with increasing order n with a separation defined by the above relation. For additional films, extra minima are superimposed at the relevant θ values. In addition to the minima, the strength of the scattering, the reflectivity, is calculated from the atomic constituents and the density so that the whole of the intensity profile is calculated for a range of reflection angles. Contamination layers, surface roughness and sample flatness all affect the intensities and minima positions. These contributions may be included in the model. The model and reflectivity data are matched by a least squares analysis to deduce relevant parameters. Unlike XPS, XRR can measure thicknesses significantly greater than 8 nm and can make measurements on multi-layer samples. The precision of the method reduces as the films get thinner since there are fewer minima and, for the thinnest films used here, there is only one minimum in the range of data. For SiO_2 on Si, the minima may not be absolute minima in the reflectivity but may be relative minima when measured against the general trend of data. Conditions may be selected to optimise this behaviour. XRR does not provide a direct chemical analysis and fitting of the reflectance data is conducted for trial models. Exactly what is fitted depends on the available software.

For XRR, PTB use the BESSY II electron storage ring since this enables the selection of the X-ray energy at 1841 eV to optimise contrast between the optical constants of SiO_2 and Si. This analysis is conducted in vacuum. At this energy, the minima are deep and sharp [1] and the use of vacuum reduces the contamination. Here, detailed components of the uncertainty are not given but the total k = 2 uncertainty is tabled at 0.10 nm for all samples from the XRR measurements. In addition, the observation of the offset of 0.49 nm, observed earlier [1,7], was considered and XRF measurements at 480 eV showed that 0.21 ± 0.02 nm of carbon were on the surface. After subtracting this from the measured values, the results given in Table 2 were obtained. The expanded uncertainty for the carbon, 0.02 nm, was added to the 0.1 nm linearly. However, in subtracting the total contamination offset of 0.49 nm, given in Table 5 from the pilot study P-38, this separate contribution (0.21 ± 0.02 nm) is ignored in generating the results in Tables 6 and 7. The uncertainties are added in quadrature.

9.3 NR

The basic principle of NR is very similar to XRR but the use of neutrons gives a scattering related to the scattering cross section of the atomic nucleus rather than the effective Z of the electron cloud. This method, as above, is conducted in vacuum. Thus, Eq (13) is valid and, again, the whole of the reflectivity curve is modelled for a depth profile of the scattering length density (SLD), including the surface and interface roughness. The model and data are matched by a least squares analysis to deduce relevant parameters. The uncertainties are deduced from the range of the values of the given parameter from all valid models returned by least squares refinement and are given at a level of 95% confidence. The values in Table 2 include an expanded uncertainty contribution of 0.21%, at a confidence level of 95%, in the neutron wavelength. The uncertainty for the angle of incidence is negligible. In the pilot study P-38 [1,13] the data were shown to exhibit an offset of 0.22 nm with respect to the XPS data, and a similar offset also appears here. In general, distinct contamination layers would show up in the SLD profiles determined by NR. However, simulations of NR reflectivities demonstrate that, if the SLD values for proposed contamination layers are within ± 15% of the SiO_2 SLD, the contamination is indistinguishable from SiO_2. Thus if the composition and density of the contamination were to result in a SLD within this range, the measured thickness of SiO_2 would include such a contamination layer. In order to match the SLD of SiO_2 with carbon containing contamination, the density and composition would have to be relatively large. One candidate that would satisfy these conditions due to its high atomic density and lack of hydrogen (which has a negative scattering length) is a carbon layer as proposed earlier with a density that is similar to that of graphite, at a roughly half a monolayer coverage. The offset given in Table 5, determined from the pilot study P-38, is thus subtracted from the data as shown in Table 6. The uncertainties are added in quadrature.

9.4 Ellipsometry

The principle of ellipsometry is similar to that of XRR in that the light reflectance intensities are measured but here the similarities end. The method is conducted in air and that has advantages of speed and, for delicate samples, sample integrity. In its most basic terms an ellipsometer measures, under specular reflection conditions, the change in the phase difference between the parallel and perpendicular components of the light beam upon reflection, Δ, and the ratios of the outgoing wave amplitudes to the incoming wave amplitudes for these components, respectively. The ratio of the latter gives tan Ψ and it is Δ and Ψ that are generally measured. For SiO_2 films, in Δ, Ψ space, it has been reported [17] that at one wavelength, the co-ordinates form a trajectory starting from $\Delta \approx 178.5^{o}$, $\Psi = 10.5^{o}$, moving, approximately, in an elliptical manner anti-clockwise. For films up to 10 nm thick, the trajectory is towards $\Delta = 150^{o}$ with less than a degree change in Ψ. The precise trajectory in Δ, Ψ space may be calculated using the known optical constants for the SiO_2 overlayer and the Si substrate. Thus, for a perfect layer of SiO_2 on Si, all of the optical parameters are known and the thickness may be determined. Issues that are not easy to address are the effects of the interface oxides, that may be small, and of the contamination overlayers, which are generally unquantified.

In the NIMT analysis, a simple 3-layer model was used with air, SiO_2 and Si with optical properties, as shown in Table 9, taken from the database supplied by the manufacturers. A number of test measurements were made leaving the samples contaminated with hydrocarbons. These contaminants were reduced with iso-propyl alcohol (IPA) as suggested

in the key comparison protocol. To remove contaminants further, the heating method of NIST was used. The samples were heated to 350 °C for 10-15 minutes and then allowed to cool for 10-15 minutes prior to measurement. On each sample, 5 locations were measured with 3 repeats at each location. This whole set of data was repeated twice more on different days, leading to a total of 45 measurements for each sample. Measurements just before and just after the heating showed a thickness reduction of 0.33 nm. Measurements comparing the first data recorded and that after cleaning showed a reduction of 0.26 nm. The materials just prior to heating were significantly more contaminated than those in the original measurements and required cleaning with IPA as noted above. These thickness reductions are consistent with those seen for this heating in the pilot study P-38 [1].

Table 9: Optical constants Used by NIMT for Ellipsometric Measurements

Wavelength	**632.8 nm**		**780.0 nm**	
Parameter	n_{opt}	k_{opt}	n_{opt}	k_{opt}
SiO_2	1.4620	0.0000	1.4590	0.0000
Si	3.8580	0.0180	3.6800	0.0063

The ellipsometry data give plots of Δ and Ψ for the two wavelengths as a function of the angle of incidence and these curves are matched to model curves with the thickness as a variable. Experimentally, it is found, as expected, that Ψ changes little for $d < 10$ nm so that the fitting is mainly for Δ. Data for the fitting in all samples shows a standard uncertainty of 0.263 nm in each fit to the model in each measurement. This is deduced from the change in d required to increase the reduced χ^2 by unity where the reduced χ^2 is determined from the difference between the data and the fitted model. Analyses of all the data lead to further standard uncertainties of 0.004 nm for the measurement repeatability, 0.012 nm for the sample uniformity and 0.028 nm for the day-to-day repeatability. The uncertainty of the optical wavelengths has an insignificant effect. The uncertainty in the optical constants in Table 9 for the oxide is important for n_{opt} but not for k_{opt} since it is zero. Extremities for n_{opt} for SiO_2 are 1.45 and 1.47. There are similar extremes for Si for both n_{opt} and k_{opt}. When all these terms are appropriately added in quadrature, the final uncertainties are about 1.0 times the uncertainty for the fit and, when expanded, average 0.533 nm, as seen in Table 2. The fit uncertainty thus dominates the final uncertainty. It is a type B uncertainty and one that does not reduce with an increase in the number of measurements. This uncertainty estimate will mainly include contributions from the inadequacy of the model. In the pilot study P-38 [1], it was interpreted that the adventitious carbonaceous contamination, adsorbed water, etc led to offsets in the range 0.45 to 1.24 nm with an average difference for measurements of packaged samples of 1.01 nm with a standard uncertainty of 0.04 nm. It was also shown that the heating used in one case led to a reduction of only 0.23 nm, with a standard deviation of the mean of 0.03 nm, from 1.22 nm. In a heating study at NPL [4], XPS measurements showed the carbon thickness to be reduced from 0.2 nm to 0.1 nm but in no cases have the contaminations been completely removed. No XPS data are available for the water contamination levels. The contamination offset evaluated in this way, from the pilot study P-38 data, is shown in Table 5. This is subtracted to give the data in Table 6. The uncertainties are added in quadrature.

10 Conclusions and how far does the light shine?

It is clear that K32 provides a set of measurements of comparable accuracies capable of measuring the amount of silicon oxide expressed as a thickness of SiO_2 on Si where the oxide layer is formed by thermal oxidation. Contamination effects observed in the pilot study P-38 have been considered and where necessary, in many cases, removed. This correction adds generally to the uncertainty for absolute thickness measurements. However, where thickness differences are required and where samples can be treated so that the contaminations are effectively the same, the significantly lower uncertainties of Table 2 may apply. For oxides prepared by routes other than thermal oxidation, which may have different densities, stoichiometries surface reactivities or other properties, the input parameters for the various methods may require change.

The uncertainties at 95% confidence, ranging from 0.05 nm to 0.3 nm as the thickness increases from 1.5 nm to 8 nm, represent a typical factor of 20 improvement on the situation prior to this overall study. To context this result, it is worth remembering that one monolayer of SiO_2 is only ~0.25 nm. Calculations of the KCRVs from the weighted mean and weighted uncertainties are shown in Table 8.

How far does the light shine in this new nanotechnology sector? From this work, it is now clear that XPS, on its own and used carefully, has excellent precision and, for SiO_2 on Si, excellent linearity for thicknesses below 8 nm. However, XPS needs a calibration of the required attenuation length (a scaling parameter) *L*. This was done here in the pilot study P-38. The present data also confirm the pilot study P-38 determination. For each new material system, a determination of the relevant attenuation length would be needed together with the extent of its constancy with thickness. With these numbers, all XPS instruments conforming to certain basic requirements and with valid software can then analyse thicknesses in those material systems, using the reference procedures established in the pilot study P-38 [1], without further calibration. So, this study provides an archetypal system on which to model further ultra-thin film measurements. In their present state, the wavelength methods have excellent precision, linearity and accuracy, apart from their sensitivity to contamination which affects the zero position in the calibration graphs for $d_{\mathrm{respondee}} = md_{\mathrm{RT}} + c$ shown in the pilot study P-38 [1] where d_{RT} = reference thickness, and c = apparent layer thickness in excess of the reference thickness extrapolated to a d_{RT} of zero. For many materials systems, and for thicknesses greater than 8 nm, apart from the zero of the scale no new data for NR or XRR may be required. Adequate data exist for many materials. It is therefore clear that, for a wide range of materials in the sub-8 nm regime, the combination of XPS and one of the wavelength methods permits full and accurate measurements to be made of the amount of material, with a valid and accurate zero value. This does not necessarily require solution to the measurement of the offset and its uncertainty in the wavelength methods since one may simply determine the attenuation length, *L*, for XPS by using thickness differences. It should be repeated that the constancy of the attenuation length with thickness needs evaluation for each system. For the calibration by a wavelength method to be conducted reliably, the contamination on all samples needs to be as similar as possible. The present cleaning methods [4] do this adequately for relatively inert materials such as SiO_2.

For films thicker than 8 nm, the contamination issue becomes of steadily reducing significance for the wavelength methods. On the other hand, for films with quantities

significantly lower than one monolayer, such as the contamination of Si wafers with metals, the length measure becomes inappropriate and data are given in atoms/m^2. For these, methods such as total reflection x-ray fluorescence (TXRF) or secondary ion mass spectrometry (SIMS) are used and calibration may be made by, for example, XRF or Rutherford backscattering spectrometry (RBS).

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Annex A
Equivalence statements

MEASURAND for thermal oxide samples: amount of silicon oxide on silicon expressed as a thickness of SiO_2.
NOMINAL VALUE: 1.5 nm on (100) Si.

Key comparison reference value (KCRV) d_R = 1.41 nm.
Uncertainty of KCRV at a level of 95% confidence, U_R = 0.09 nm.

The KCRV was calculated as a weighted mean of the results. The uncertainty was calculated at 95% confidence.

The degree of equivalence of each laboratory with respect to the KCRV is given by a pair of numbers: $D_i = d_i - d_R$ and its expanded uncertainty U_i at 95% confidence.

	D_i nm	U_i nm
NIMT	-0.21	0.67
CSIR-NML	-0.06	0.13
NRCCRM	0.04	0.11
NPL	-0.03	0.09
BAM	0.07	0.10
KRISS	-0.04	0.10
NIST	0.14	0.28

MEASURAND for thermal oxide samples: amount of silicon oxide on silicon expressed as a thickness of SiO_2.
NOMINAL VALUE: 2 nm on (100) Si.

Key comparison reference value (KCRV) d_R = 1.84 nm.
Uncertainty of KCRV at a level of 95% confidence, U_R = 0.10 nm.

The KCRV was calculated as a weighted mean of the results. The uncertainty was calculated at 95% confidence.

The degree of equivalence of each laboratory with respect to the KCRV is given by a pair of numbers: $D_i = d_i - d_R$ and its expanded uncertainty U_i at 95% confidence.

	D_i nm	U_i nm
NIMT	-0.30	0.67
CSIR-NML	-0.14	0.16
NRCCRM	0.06	0.14
NPL	-0.03	0.11
BAM	0.09	0.13
KRISS	-0.01	0.12

MEASURAND for thermal oxide samples: amount of silicon oxide on silicon expressed as a thickness of SiO_2.
NOMINAL VALUE: 3 nm on (100) Si.

Key comparison reference value (KCRV) d_R = 3.23 nm.
Uncertainty of KCRV at a level of 95% confidence, U_R = 0.15 nm.

The KCRV was calculated as a weighted mean of the results. The uncertainty was calculated at 95% confidence.

The degree of equivalence of each laboratory with respect to the KCRV is given by a pair of numbers: $D_i = d_i - d_R$ and its expanded uncertainty U_i at 95% confidence.

	D_i nm	U_i nm
NIMT	-0.18	0.68
CSIR-NML	-0.09	0.24
NRCCRM	0.05	0.22
PTB	-0.11	0.35
NPL	-0.01	0.16
KRISS	0.06	0.19

MEASURAND for thermal oxide samples: amount of silicon oxide on silicon expressed as a thickness of SiO_2.
NOMINAL VALUE: 4 nm on (100) Si.

Key comparison reference value (KCRV) d_R = 3.97 nm.
Uncertainty of KCRV at a level of 95% confidence, U_R = 0.16 nm.

The KCRV was calculated as a weighted mean of the results. The uncertainty was calculated at 95% confidence.

The degree of equivalence of each laboratory with respect to the KCRV is given by a pair of numbers: $D_i = d_i - d_R$ and its expanded uncertainty U_i at 95% confidence.

	D_i nm	U_i nm
NIMT	-0.20	0.68
CSIR-NML	-0.10	0.27
NRCCRM	0.05	0.25
PTB	0.03	0.35
NPL	-0.02	0.17
KRISS	0.11	0.23
NIST	-0.02	0.31

MEASURAND for thermal oxide samples: amount of silicon oxide on silicon expressed as a thickness of SiO_2.
NOMINAL VALUE: 8 nm on (100) Si.

Key comparison reference value (KCRV) d_R = 7.65 nm.
Uncertainty of KCRV at a level of 95% confidence, U_R = 0.27 nm.

The KCRV was calculated as a weighted mean of the results. The uncertainty was calculated at 95% confidence.

The degree of equivalence of each laboratory with respect to the KCRV is given by a pair of numbers: $D_i = d_i - d_R$ and its expanded uncertainty U_i at 95% confidence.

	D_i nm	U_i nm
NIMT	-0.03	0.72
CSIR-NML	0.04	0.41
NRCCRM	-0.38	0.49
PTB	-0.11	0.41
NPL	0.02	0.29
KRISS	0.17	0.42

MEASURAND for thermal oxide samples: amount of silicon oxide on silicon expressed as a thickness of SiO_2.
NOMINAL VALUE: 2 nm on (111) Si.

Key comparison reference value (KCRV) d_R = 1.71 nm.
Uncertainty of KCRV at a level of 95% confidence, U_R = 0.11 nm.

The KCRV was calculated as a weighted mean of the results. The uncertainty was calculated at 95% confidence.

The degree of equivalence of each laboratory with respect to the KCRV is given by a pair of numbers: $D_i = d_i - d_R$ and its expanded uncertainty U_i at 95% confidence.

	D_i nm	U_i nm
NIMT	-0.18	0.67
CSIR-NML	-0.07	0.17
NRCCRM	0.06	0.14
NPL	-0.01	0.12
BAM	-0.02	0.13
NIST	0.12	0.29

MEASURAND for thermal oxide samples: amount of silicon oxide on silicon expressed as a thickness of SiO_2.
NOMINAL VALUE: 3 nm on (111) Si.

Key comparison reference value (KCRV) d_R = 3.27 nm.
Uncertainty of KCRV at a level of 95% confidence, U_R = 0.18 nm.

The KCRV was calculated as a weighted mean of the results. The uncertainty was calculated at 95% confidence.

The degree of equivalence of each laboratory with respect to the KCRV is given by a pair of numbers: $D_i = d_i - d_R$ and its expanded uncertainty U_i at 95% confidence.

	D_i nm	U_i nm
NIMT	-0.14	0.69
CSIR-NML	-0.07	0.25
NRCCRM	0.03	0.24
PTB	-0.04	0.36
NPL	0.01	0.19

MEASURAND for thermal oxide samples: amount of silicon oxide on silicon expressed as a thickness of SiO_2.
NOMINAL VALUE: 5 nm on (111) Si.

Key comparison reference value (KCRV) d_R = 5.27 nm.
Uncertainty of KCRV at a level of 95% confidence, U_R = 0.20 nm.

The KCRV was calculated as a weighted mean of the results. The uncertainty was calculated at 95% confidence.

The degree of equivalence of each laboratory with respect to the KCRV is given by a pair of numbers: $D_i = d_i - d_R$ and its expanded uncertainty U_i at 95% confidence.

	D_i nm	U_i nm
NIMT	-0.08	0.70
CSIR-NML	-0.08	0.30
NRCCRM	0.01	0.34
PTB	0.05	0.37
NPL	-0.01	0.21
NIST	0.14	0.33

MEASURAND for thermal oxide samples: amount of silicon oxide on silicon expressed as a thickness of SiO_2.
NOMINAL VALUE: 6 nm on (111) Si.

Key comparison reference value (KCRV)
d_R = 6.18 nm.
Uncertainty of KCRV at a level of 95% confidence, U_R = 0.25 nm.

The KCRV was calculated as a weighted mean of the results. The uncertainty was calculated at 95% confidence.

The degree of equivalence of each laboratory with respect to the KCRV is given by a pair of numbers: $D_i = d_i - d_R$ and its expanded uncertainty U_i at 95% confidence.

	D_i nm	U_i nm
NIMT	0.00	0.71
CSIR-NML	-0.03	0.35
NRCCRM	-0.09	0.49
PTB	-0.05	0.40
NPL	0.01	0.26

Annex B
NMIJ XPS and XRR Data

Annex B reports measurement data from NMIJ that were withdrawn from the KCRV evaluation. The NMIJ XRR data and uncertainties are related to a measurand different from that defined for K32 in 2.1, and the XPS data have been measured at a different geometry.

B.1 The NMIJ measurements

The data reported in Table 2 are shown in Table B.1 to show the measurement method.

Table B.1: Results for the equivalent thicknesses of SiO_2 and their associated uncertainties; *d* = thickness, *U* = uncertainty for a 95% confidence interval. These are for individual samples and for comparison need correcting to a reference sample. (* = XPS data)

(100) material									
"1.5 nm"		"2 nm"		"3 nm"		"4 nm"		"8 nm"	
d nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm
1.28*	0.62*	1.83*	0.62*	3.57	0.17	4.53	0.11	7.93	0.09

(111) material							
"2 nm"		"3 nm"		"5 nm"		"6 nm"	
d nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm
1.67*	0.62*	3.89	0.08	5.91	0.26	6.83	0.07

For the comparison of data, as noted at 6, the sample to sample differences shown in Tables 4 and B.2 need inclusion.

Table B.2: NMIJ individual sample thickness, nm, minus the thickness of a reference sample, nm, for each nominal thickness, as determined in the original ellipsometry maps.

(100) material					(111) material			
1.5nm	2nm	3nm	4nm	8nm	2nm	3nm	5nm	6nm
-0.004	-0.026	-0.003	-0.006	-0.135	0.011	0.012	-0.030	0.034

This leads to the results in Table B.3, as shown in Fig. 1.

Table B.3: Results for the equivalent thicknesses of SiO_2 and their associated uncertainties; *d* = thickness, *U* = uncertainty for a 95% confidence interval. These are for individual samples and for comparison have been corrected to a reference sample. (* = XPS data)

(100) material									
"1.5 nm"		"2 nm"		"3 nm"		"4 nm"		"8 nm"	
d nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm
1.284*	0.623*	1.856*	0.623*	3.573	0.180	4.536	0.125	8.065	0.108

(111) material							
"2 nm"		"3 nm"		"5 nm"		"6 nm"	
d nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm	*d* nm	*U* nm
1.659*	0.623*	3.878	0.100	5.940	0.267	6.796	0.092

B.2 Analysis of Uncertainties

B.2.1 XPS

For XPS, NMIJ used a commercial V G Scientific ESCALAB 220i-XL instrument with monochromated Al Kα X-rays applying the two-peak method of Eq (5) with the emitted electrons detected along the surface normal instead of the reference geometry emission angles. The value of R_o was determined from the data of I_{SiO_2} and I_{Si}, using the relation:

$$I_{SiO_2} = R_o \left(I_{SiO_2} - I_{Si} \right) \quad \text{(B.1)}$$

to be 0.732 ± 0.012 (standard uncertainty). To use Eq (5), a value of L is required for this geometry and here this is deduced to be 3.626 ± 0.023 nm (standard uncertainty) from Eq (5) itself by measuring d by XRR for the thicker samples. In this procedure, R_o is lower and L is higher than the values used by the other participants for evaluation of XPS data. The use of normal emission along a crystal axis leads to an enhanced substrate emission (forward focussing) that may explain the lower value of R_o. This enhancement will decay as the thickness increases [1]. The uncertainty estimate is made from Eq (11) with U_E, U_A, U_P and U_F as zero and U_L as 1.1%, deduced from the standard uncertainty of 0.023 nm in the derived value of 3.626 nm. The value of U_n is deduced from the standard deviation in the scatters for the 6 repeat measurements which, combined with the 1.6% standard uncertainty in R_o, leads to a standard uncertainty of 0.09 in the expression $\ln(1+I_{SiO_2}/R_o I_{Si})$ such that U_n is 0.18λ. Finally a standard uncertainty of 0.06 nm is added for the uniformity of the samples. No contribution is allowed for U_θ since any error at 0° emission is unimportant. The overall uncertainty is dominated by the spectral measurement contribution in $\ln(1+I_{SiO_2}/R_o I_{Si})$ which, for the three thinnest films measured in K32, ranges from 35% to 50% at k = 2. A significant part of this uncertainty arises from the low signal levels used. The uncertainties are listed in Table B.1, shown with an asterisk.

B.2.2 XRR

For XRR, NMIJ used a commercial instrument with a Cu Kα source [16,17]. For the analysis of uncertainties, NMIJ used a relation similar to Eq (11) and took into account the following standard uncertainties. First there is a standard uncertainty of 0.001 nm to 0.003 nm in d from the standard uncertainty in the 0.154 nm wavelength, λ. This contributed around 0.04%. Next, standard uncertainties of 0.01 nm arose equally from the measurement of θ and the sample flatness. From the repeatability of 6 measurements on each sample, a standard uncertainty of 0.08 nm was found for the thinnest film and 0.04 nm for the thickest. An additional standard uncertainty of 0.02 to 0.01 nm was added for unknowns in the analysis method. In the analysis, the thickness of the carbonaceous overlayer was estimated by XPS as 0.1 nm and 0.05 nm, half of the carbonaceous overlayer thickness, was subtracted from the SiO_2 thickness as an approximation to the equivalent thickness since the organic overlayer has a density about half that of SiO_2. The associated uncertainties were stated to be 0.01 nm. The stated uncertainties are dominated by the repeatability of the 6 measurements. Here, the expanded standard deviation has been used. The above uncertainties are combined in quadrature and then expanded with $k = 2$ to give the uncertainties listed in Table B.1. For the K32 samples, in addition to the hydrocarbon contamination on the surface there is also water bonded to the surface when measurements are made in the ambient atmosphere. It is the view of NMIJ that a correction and uncertainty for a water layer are not required.

An offset of 0.3 to 0.4 nm is observable between the NMIJ XRR data and the KCRVs. This is similar to the offset observed in the pilot study within the experimental repeatability.

CCQM-K32

SURFACE ANALYSIS
COMPARISON OF SiO_2 ON Si MEASUREMENTS

A key comparison for the Consultative Committee on Amount of Substance

Protocol for the Measurements

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27 April 2005

CCQM-K32
SURFACE ANALYSIS
Thickness of SiO_2 on Si in the range 1.5 nm to 8 nm
A key comparison in the Consultative Committee on Amount of Substance

Protocol for the Measurements

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Contents

1 OBJECTIVE……………………………………………………………………32
2 TIMETABLE………………………………………………………………… 32
3 THIS PACKAGE………………………………………………………………32
4 THE MATERIAL…………………………………………………………… 33
5 SAMPLE HANDLING………………………………………………………34
6 PRACTICAL ISSUES IN MEASURING THE OXIDE THICKNESS……………..34
7 REPORTING THE RESULTS AND CALCULATING THE THICKNESS……....35
8 ANY DOUBTS………………………………………………………………..36
Annex A – Sample Cleaning (if required)………………………………………37
Annex B – Table to aid reporting components of uncertainty measurement…..……….38

1 OBJECTIVE

The measurand in this study is the thickness of the silicon oxide layer on each of a total of 9 samples of nominal thicknesses in the range 1.5 to 8 nm on (100) and (111) Si substrates, expressed as the thickness of SiO_2. The measurements are to be accompanied by estimates of the uncertainties at a confidence level of 95%, deduced from the standard uncertainties. These will provide the basis to establish the degree of equivalence between laboratories and the extent to which the results are traceable to the SI.

The "Guidelines for CIPM key comparisons", which this protocol follows, may be found at: http://www.bipm.org/utils/en/pdf/guidelines.pdf

2 TIMETABLE

You should complete the analyses required for this work within approximately five calendar months of receipt of this package. The deadline for receipt of the data is 18 September 2005.

3 THIS PACKAGE

This package, unless you have otherwise specified, contains this protocol and a set of 9 Fluoroware containers, each containing one sample. Inspect the packaging to check if it has been opened by customs and if the integrity of the samples has been compromised. If you are

in doubt, the samples may either be cleaned as described in the Annex or new samples requested. Please notify us that everything is received in order:

☐ I have emailed NPL that all is OK with the samples on ___/___/2005.

4 THE MATERIAL

The materials for analysis in the standard set comprise one piece of each of the nominal thicknesses 1.5 nm, 2 nm, 3 nm, 4 nm and 8 nm of SiO_2 on Si for (100) substrates and 2 nm, 3 nm, 5 nm and 6 nm of SiO_2 on Si for (111) substrates. The 9 pieces of material are each supplied in separate containers to maintain their identity and integrity.

Your sample codes are given in the covering letter in a completed table of the form:

Serial Numbers of Your Samples

(100) Surface, Nominal Oxide Thicknesses					Sample Size	
1.5 nm	2 nm	3 nm	4 nm	8 nm	Regular	Special

(111) Surface, Nominal Oxide Thicknesses				Sample Size	
2 nm	3 nm	5 nm	6 nm	Regular	Special

The material, unless you have otherwise specified, is approximately 1 cm^2 in area, with nominal thickness 525 µm, polished on one side to better than 1 nm rms roughness. Your measurements are to be on this polished side. The wafers are intended to be within 1° of the (100) or the (111) surfaces. The material is cleaved along (111) planes so that the (100) material is a square of side 10 mm bounded by <110> directions, whereas the (111) material is provided as a triangle of side 15 mm, also bounded by <110> directions. The scribing for cleaving leaves very small fragments of Si adjacent to the edges of the samples. This has largely been removed by a washing and ultrasonic procedure using HPLC quality (>99.5%) isopropyl alcohol. Furthermore, these samples have not been packaged in a clean room environment. Inspection shows that approximately 100 particles remain per mm^2.

Analyses show that these and all such materials accumulate organics, hydrocarbons, silanes and phthalates from the environment. During storage, this thickness increases to around 0.35 nm on the polished surface, in normal, uncirculated laboratory air after 100 days, but that this is kept below 0.2 nm in the container supplied, provided it is not exposed to excessive heat. If necessary, the contamination may be reduced to a thickness of about 0.14 nm by cleaning as described in the Annex. If your measurement method is affected by the presence of contamination, you should consider the use of one of these cleaning methods.

Furthermore, it is known that SiO_2 and these contamination layers, respectively, adsorb and absorb H_2O. If your measurement method is affected by contamination, you may need to take relevant action.

Do not unpack these samples until you are nearly ready to analyse them. Before doing so, read the rest of this protocol so that you are clear about the next steps.

5 SAMPLE HANDLING

You will have a sample handling procedure in your quality system relating to this measurand and should use that procedure. The following comments, from the pilot study, were found helpful by participants.

The samples have no identifying marks and are only identified by the container label and the sample shape. If you intend to analyse the samples one by one, by mounting them on the same sample holder, it is good practice to keep the samples in their containers and remove them only if you need to clean them and for this mounting. If you mount them together on one sample holder, ensure that their identities are maintained. If you need to reduce the size of the samples, you may do this by traditional wafer dicing or other methods that maintain the integrity of the polished surface. If you do this, note the above issues relating to particulates.

Inspect the samples for any scratches, blemishes or marks on the polished surfaces. Finger marks should be avoided but may be removed as described in the Annex. Note the condition of the surface. It should be featureless.

You may have sophisticated sample handling procedures as routine in your laboratory. Keep to those procedures but ensure that they are always superior to the minimum level given below.

You may need to handle the samples using stainless steel tweezers. If so, grip the sample at the edge only, in a region that will not be analysed. Avoid breathing or speaking over the samples. Use the tweezers that were provided in the pilot study or tweezers that are of uncoated stainless steel. Immerse the tweezers before use for 16 hours in HPLC grade (>99.5%) isopropyl alcohol (IPA). Next, remove the liquid, renew the IPA, agitate ultrasonically for 1 minute, rinse in fresh IPA and remove the excess liquid using a gas jet of pure dry argon. Alternatively, boil the tweezers in ultra-high purity water for 10 minutes. Use polythene gloves, or gloves of a higher quality, to avoid contaminating the tweezers or your cleaning equipment with finger grease. Do not use moulded gloves, for example vinyl, which will probably be covered with highly contaminating release agents. Keep these tweezers in a clean, glass container for future use.

6 PRACTICAL ISSUES IN MEASURING THE OXIDE THICKNESS

Reduce the sample’s lateral dimensions, if necessary, and remove any dust or particulate matter generated in that process [use, for instance, the argon gas jet etc, as noted in the Annex, but do not use a method likely to contaminate the sample]. If your measurement method is sensitive to contamination, use the cleaning procedure discussed in the Annex. If you are using your own cleaning procedure, observe any stabilisation period etc.

Ensure that any necessary instrument calibrations are up to date.

Conduct your analyses of the 9 samples. In many key comparisons, 6 measurements are made for each sample. The number of replicate measurements that you make and the number of samples on which you conduct replicate measurements are a matter of your judgement in relation to the analytical time and the accuracy to which you wish to work.

Try to ensure that your analyses are in the central regions of the samples. Do not acquire data within 1 mm of the sample edge. Note the order of analysis of the samples. Ensure, if possible, that the signal collection time is sufficient that the signal levels you measure are high enough to contribute an insignificant uncertainty to the final derivation of the thickness. Note all of the instrumental parameters used.

After analysing the samples, if your samples have not been consumed by your procedures and if the original surfaces still exist, note the condition of the surfaces. They should still be featureless. Record any beam marks. Return the samples to their containers and store them in a cool place in case any anomalies in the data are found when compiling the draft A.

7 REPORTING THE RESULTS AND CALCULATING THE THICKNESS

Report the amount of silicon oxide as a thickness of silicon dioxide. It is a requirement of key comparisons the measurements are accompanied by estimates of the uncertainties in accordance with the ISO Guide to the Expression of Uncertainty in Measurement (GUM). Here, we ask for uncertainty at a confidence level of 95%.

It may be helpful to report the initial and final state of the sample, any cleaning or other preparation, as appropriate.

Report your analytical method, together with relevant calibration data and experimental details. Report the measurement data and supporting data. Report any repeat data and associated statistics.

Describe the evaluation of the 9 thicknesses and tabulate the thicknesses that you obtain. List the values and source of relevant input parameters to the equation(s) generating the measurand result. List, also, the principal components of the uncertainty contributions [e.g. statistics of the data, fitting of the model, density, refractive index, angles, wavelengths, etc – these should include any type A (statistical) and Type B (systematic or biases) contributions] The table in Annex B may be used to help here. Combine the uncertainty contributions according to ISO GUM in order to obtain the relevant uncertainty. Evaluate the number of degrees of freedom in the information, if necessary, and provide an expanded uncertainty at a confidence level of 95%. Please use a expansion factor of 2 unless you have reason to use a different number (for distributions that are not Gaussian, other expansion factors are required).

Table of Reported Data

(100) Surface, Nominal Oxide Thicknesses	**1.5 nm**	**2 nm**	**3 nm**	**4 nm**	**8 nm**
Thickness of silicon oxides as silicon dioxide thickness, nm					
Uncertainty at 95% confidence level, nm					

(111) Surface, Nominal Oxide Thicknesses	**2 nm**	**3 nm**	**5 nm**	**6 nm**
Thickness of silicon oxides as silicon dioxide thickness, nm				
Uncertainty at 95% confidence level, nm				

☐ Method reported to NPL on ___/___/2005.
☐ Thicknesses reported to NPL on ___/___/2005.
☐ Uncertainties reported to NPL on ___/___/2005.

These samples essentially comprise an even layer of amorphous SiO_2 on single crystal Si. At the SiO_2/Si interface, the thicknesses of the interface oxides have been measured on similar samples to be below 0.15 nm. The existence of an interface may need to be included in any model that you use. At the outer surface, there will be adsorbed hydrocarbons, organics etc as well as water that may or may not need to be included in your model.

Send your report either hardcopy or electronically to:
M P Seah, DQL, National Physical Laboratory, Teddington, Middlesex TW11 0LW, UK
[Tel: +44 20 8943 6634; Fax: +44 20 8943 6453; email: martin.seah@npl.co.uk]

8 ANY DOUBTS

If you are unsure of anything, please contact the project leader, M P Seah, email: martin.seah@npl.co.uk.

Annex A – Sample Cleaning (if required)

The following method has been evaluated at NPL over several years and has been found to be effective. No significant change in the oxide thickness has been seen at NPL for multiple cleanings. No significant changes in the thickness should therefore occur. More aggressive cleaning methods may increase or decrease the oxide thickness. A compilation of cleaning methods, "Ultra-thin SiO_2 on Si: I, Quantifying and Removing Carbonaceous Contamination" is published by M P Seah and S J Spencer in Journal of Vacuum Science and Technology A21 345-352 (2003).

Only clean the samples if you have evidence that they need cleaning. Either clean the samples as described below or use your own documented method if that is part of a method that you have established as part of a measurement traceability procedure.

Procure a number of test tubes equal to the number of samples to be cleaned. Ensure that these test tubes are clean and dry. You may clean the test tubes by immersing them in boiling ultra-high purity water for 1 hour. Immerse each sample to be cleaned in a separately labelled tube in HPLC quality (>99.5%) isopropyl alcohol (IPA) for 16 hours (e.g. overnight). The top of the test tube may be conveniently closed by a piece of clean aluminium foil. Next, remove the liquid, renew the IPA, agitate ultrasonically for 1 minute, rinse in fresh IPA and remove the excess liquid using a gas jet of pure dry argon. Record your actions. The samples are now ready for use.

NOTE 1 The procedure using 16 hours immersion in solvent leaves significantly less carbon than a simple ultrasonic rise.

NOTE 2 If IPA is not available you may use HPLC quality chloroform or dichloromethane but the level of carbon remaining is generally about twice as much as for IPA. However, the amount left depends on how the samples have been contaminated in the first place. Note that there are relevant safety requirements in using all solvents. Carbon deposited during any spectroscopic analysis may be cross linked, if radiation is used, to form a tough adherent layer which cannot be removed without compromising the oxide integrity. Do not use other cleaning methods, although they may be known to remove contamination, since they may also change the oxide thickness.

NOTE 3 If pure dry argon is not available, pure dry inert gases or nitrogen may be used to blow liquid off the samples. Do not use gas from pressurised cans that include a propellant or from compressed air lines that may contain oil vapour. Ensure that you comply with relevant safety requirements.

NOTE 4 Under no circumstances use any proprietary cleaning agents or liquids containing surfactants.

Annex B - Table to aid reporting components of uncertainty of measurement

SiO_2 sample with a nominal thickness of ___ nm

Identification: ____

Equations used: $d =$ ....

$u^2(d) =$ ....

quantity X_i	estimate x_i	uncertainty $u(x_i)$	probability distribution	sensitivity coefficient c_i	uncertainty contribution $u_i(h)$	degrees of freedom v_i

For the type of probability distribution please use: N = normal; R = rectangular; T = triangular; U = U-shaped.

SiO_2 thickness: $d =$

Combined standard uncertainty: $u_c(d) =$

Effective degree of freedom: $v_{eff}(d) =$

Expanded uncertainty: $U(k=2)=$ with a coverage factor k=2

Laboratory: ....

Date: .... Signature:...