NPL
National Physical Laboratory

NPL REPORT ENG 62

# EMRP SIB05 DELIVERABLE 1.1.3
# EVALUATION OF HEAT TREATED SILICON SAMPLES FOR SURFACE PROPERTIES AND CHARGE RETENTION.

STUART DAVIDSON

DEC 2015

# Deliverable 1.1.3 Evaluation of heat treated silicon samples for surface properties and charge retention.

Stuart Davidson
Engineering Measurement Division

ISSN 1754-2987

National Physical Laboratory
Hampton Road, Teddington, Middlesex, TW11 0LW

Approved on behalf of NPLML by
Andrew Lewis
Knowledge Leader, Engineering Measurement Division

# CONTENTS

# 1 INTRODUCTION

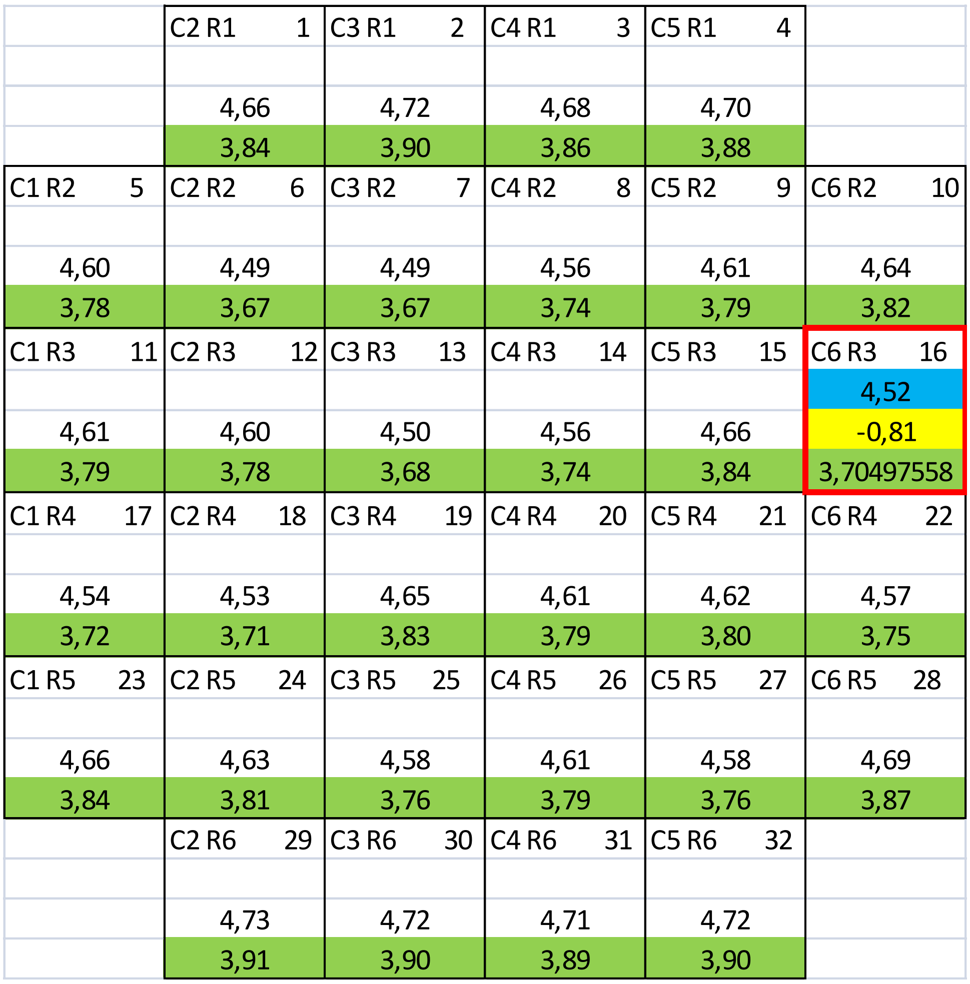
The European Metrology Research Programme (EMRP) Project SIB-05 (NewKILO) addresses the requirements for the practical implementation of the redefinition of the SI unit of the kilogram. Within the Project the aim of this Deliverable was to investigate the surface hardness and charge retention of silicon samples with native and thermally grown oxides surface layers, this report describes the tests undertaken and results produced to achieve this. Silicon has many of the properties required for the watt balance experiment and is used in for the realisation of the kilogram in the Avogadro project. This material has the potential advantage that natural oxides can be grown immediately on the silicon surface, which protect the surface from the surrounding environment. The surface properties of materials used for mass standards is critical in influencing the long-term mass stability and therefore the ultimate performance of the artefact. This Deliverable aimed to determine whether any differences in surface hardness between native and thermal oxides of different thicknesses could be determined.

The growth of (native or thermal) oxides on the surface of silicon artefacts additionally raises issues with static charge accumulation and retention. Silicon dioxide is an extremely good insulator providing charge retention times of tens of years to electronic devices. This could pose problems for mass determination and effective stability so the static properties of silicon artefacts will be investigated with a view to characterising and minimising its effect on mass measurement. This Deliverable aimed to determine whether the type or thickness of the oxide layer influenced the accumulation of charge on silicon artefacts and additionally the ease with which accumulated charge could be dissipated.

# 2 SAMPLE PREPARATION

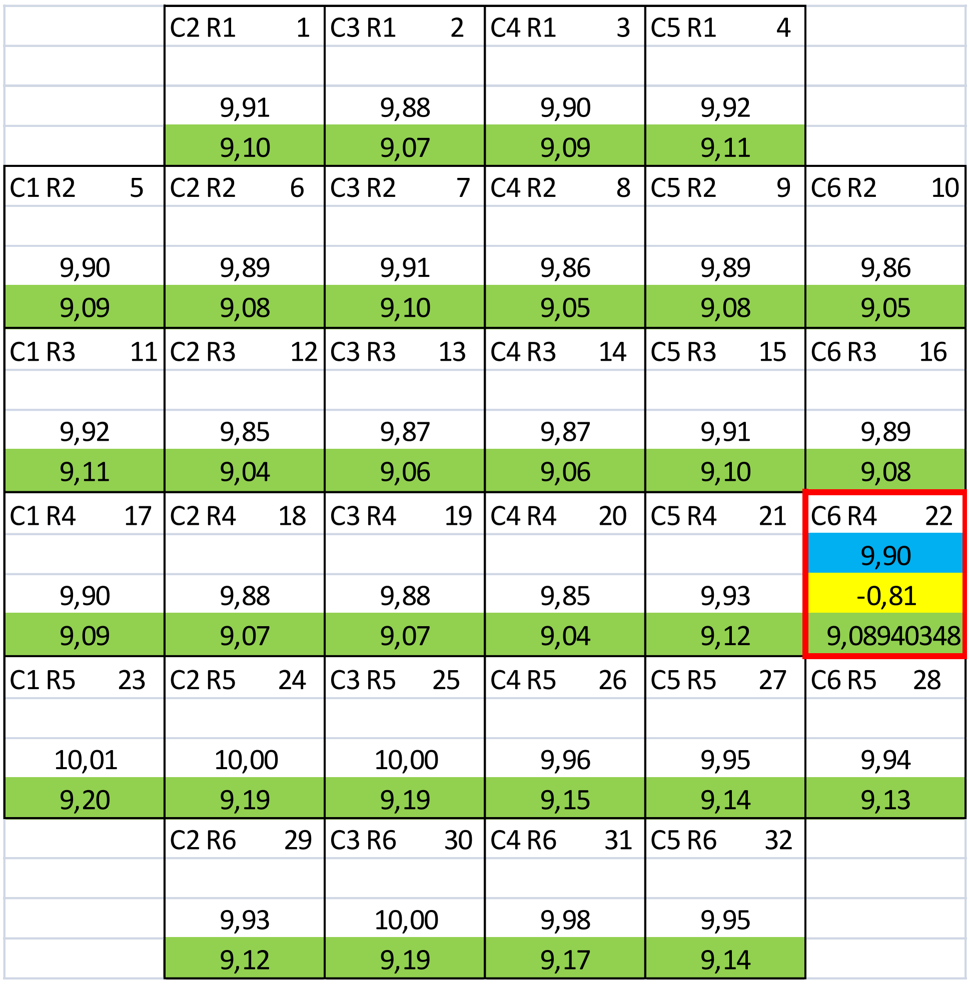
Three single crystal silicon wafers were used, one was left with only the native oxide in place and thermal oxides of nominal thickness 5 nm and 10 nm were grown on the other wafers. The thickness of the thermally generated oxides were determined using a Charged Couple Device (CCD).

The Figures 1 and 2 show the results of $SiO_2$ film thickness measurements using the CCD for the 5 nm and 10 nm oxide thickness wafers, respectively. All samples have been identified by column and row numbers (*e.g.* C2 R1) and are also numbered consecutively. At the red highlighted positions additional reference measurements with the photomultiplier tube (PMT) were carried out, with reference to a calibrated (oxide thickness) standard. The blue marked value is the CCD raw value at this point and the yellow marked value is the resulting calibration factor stemming from calibration with the PMT reference standard. The green marked values for the other cells are the calculated thickness at the position taking into account the calibration factor. The unmarked values are the raw values for CCD. All thickness values are in given in nanometres.



| | | | | | |
|---|---|---|---|---|---|
| | C2 R1 1 | C3 R1 2 | C4 R1 3 | C5 R1 4 | |
| | | | | | |
| | 4,66 | 4,72 | 4,68 | 4,70 | |
| | 3,84 | 3,90 | 3,86 | 3,88 | |
| C1 R2 5 | C2 R2 6 | C3 R2 7 | C4 R2 8 | C5 R2 9 | C6 R2 10 |
| | | | | | |
| 4,60 | 4,49 | 4,49 | 4,56 | 4,61 | 4,64 |
| 3,78 | 3,67 | 3,67 | 3,74 | 3,79 | 3,82 |
| C1 R3 11 | C2 R3 12 | C3 R3 13 | C4 R3 14 | C5 R3 15 | C6 R3 16 |
| | | | | | 4,52 |
| 4,61 | 4,60 | 4,50 | 4,56 | 4,66 | -0,81 |
| 3,79 | 3,78 | 3,68 | 3,74 | 3,84 | 3,70497558 |
| C1 R4 17 | C2 R4 18 | C3 R4 19 | C4 R4 20 | C5 R4 21 | C6 R4 22 |
| | | | | | |
| 4,54 | 4,53 | 4,65 | 4,61 | 4,62 | 4,57 |
| 3,72 | 3,71 | 3,83 | 3,79 | 3,80 | 3,75 |
| C1 R5 23 | C2 R5 24 | C3 R5 25 | C4 R5 26 | C5 R5 27 | C6 R5 28 |
| | | | | | |
| 4,66 | 4,63 | 4,58 | 4,61 | 4,58 | 4,69 |
| 3,84 | 3,81 | 3,76 | 3,79 | 3,76 | 3,87 |
| | C2 R6 29 | C3 R6 30 | C4 R6 31 | C5 R6 32 | |
| | | | | | |
| | 4,73 | 4,72 | 4,71 | 4,72 | |
| | 3,91 | 3,90 | 3,89 | 3,90 | |

**Figure 1: $SiO_2$ film thicknesses (nm) for the 5 nm (nom.) wafers (see text for colour key).**



| | | | | | |
|---|---|---|---|---|---|
| | C2 R1 1 | C3 R1 2 | C4 R1 3 | C5 R1 4 | |
| | | | | | |
| | 9,91 | 9,88 | 9,90 | 9,92 | |
| | 9,10 | 9,07 | 9,09 | 9,11 | |
| C1 R2 5 | C2 R2 6 | C3 R2 7 | C4 R2 8 | C5 R2 9 | C6 R2 10 |
| | | | | | |
| 9,90 | 9,89 | 9,91 | 9,86 | 9,89 | 9,86 |
| 9,09 | 9,08 | 9,10 | 9,05 | 9,08 | 9,05 |
| C1 R3 11 | C2 R3 12 | C3 R3 13 | C4 R3 14 | C5 R3 15 | C6 R3 16 |
| | | | | | |
| 9,92 | 9,85 | 9,87 | 9,87 | 9,91 | 9,89 |
| 9,11 | 9,04 | 9,06 | 9,06 | 9,10 | 9,08 |
| C1 R4 17 | C2 R4 18 | C3 R4 19 | C4 R4 20 | C5 R4 21 | C6 R4 22 |
| | | | | | 9,90 |
| 9,90 | 9,88 | 9,88 | 9,85 | 9,93 | -0,81 |
| 9,09 | 9,07 | 9,07 | 9,04 | 9,12 | 9,08940348 |
| C1 R5 23 | C2 R5 24 | C3 R5 25 | C4 R5 26 | C5 R5 27 | C6 R5 28 |
| | | | | | |
| 10,01 | 10,00 | 10,00 | 9,96 | 9,95 | 9,94 |
| 9,20 | 9,19 | 9,19 | 9,15 | 9,14 | 9,13 |
| | C2 R6 29 | C3 R6 30 | C4 R6 31 | C5 R6 32 | |
| | | | | | |
| | 9,93 | 10,00 | 9,98 | 9,95 | |
| | 9,12 | 9,19 | 9,17 | 9,14 | |

**Figure 2: $SiO_2$ film thicknesses (nm) for the 10 nm (nom.) wafers (see text for colour key).**

.

The expanded uncertainty ($k = 2$) for the calibrated values is $U(d)$ = 1.0 nm. The variation of the measured thicknesses varies from 0.23 nm (5-nm-wafer) to 0.16 nm (10-nm-wafer). Due to the given uncertainty a constant thickness value for both wafers may be assumed. The crystals were divided up into 10 mm squares and these were used for the analysis described.

# 3 SAMPLE MEASUREMENT

## 3.1 SURFACE HARDNESS DETERMINATION

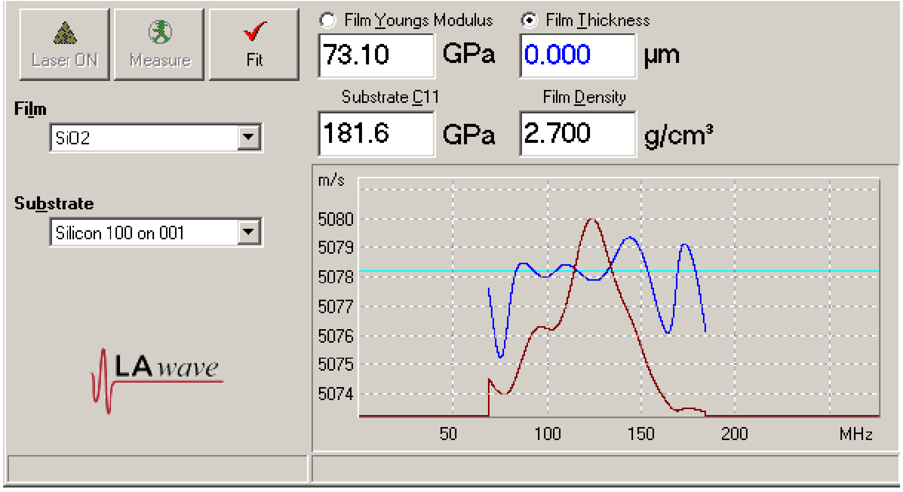
Due to thinness of the oxide layers on the surface of the samples the use of conventional (nano-) indentation and instrumented indenter hardness measurement techniques did not give satisfactory results. A technique using surface acoustic waves was also tried as a means of determining the surface properties of the silicon samples and this was more successful.

### 3.1.1 Surface Acoustic Wave Measurement

Surface acoustic waves are elastic vibrations, with nanometre amplitude, propagating along the surface of a material. The amplitude is highest at the surface and decays within the material exponentially. This distance to the surface is defined as the penetration depth of the surface acoustic wave. The penetration depth goes down with increasing frequency. Due to the exponential decay of the amplitude, the wave energy is concentrated at the surface, making the wave propagation very sensitive to thin films and to micro-structural variations just beneath the surface of a material. For a homogeneous sample the wave velocity is constant but with thin films (of thickness less than a few percent of the penetration depth) the propagation velocity of the wave depends on frequency. This phenomenon is termed dispersion.

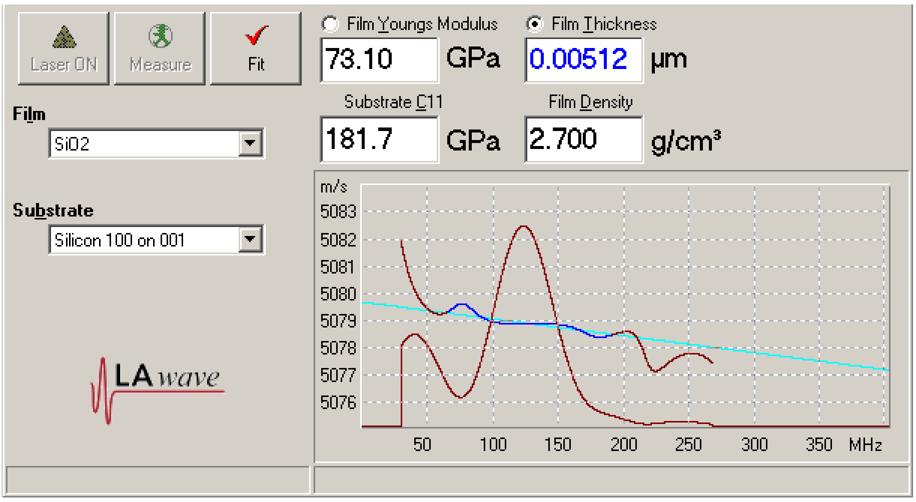
An LAwave laser-acoustic instrument was used to test the samples. It is an ultrasonic technique making use of the dispersion of surface acoustic waves. The device measures the dispersion spectrum and calculates the material parameters of the film material by fitting a dispersion curve deduced from the theory of surface acoustic wave dispersion.

In order to calculate the Young’s modulus ($E$) of the surface layer of the silicon samples a value for the film (oxide) thickness need to be used. For the sake of this investigation the (thermal) oxide thicknesses were assumed to be as reported in Section 2 of this report. The oxide thickness on the natural silicon sample was assumed to be zero.  The value of Young’s modulus for the substrate (silicon 110 orientation) was assumed to be 181.6 GPa. The results of the measurements using the LAwave instrument and software are shown in Figures 3 to 5.



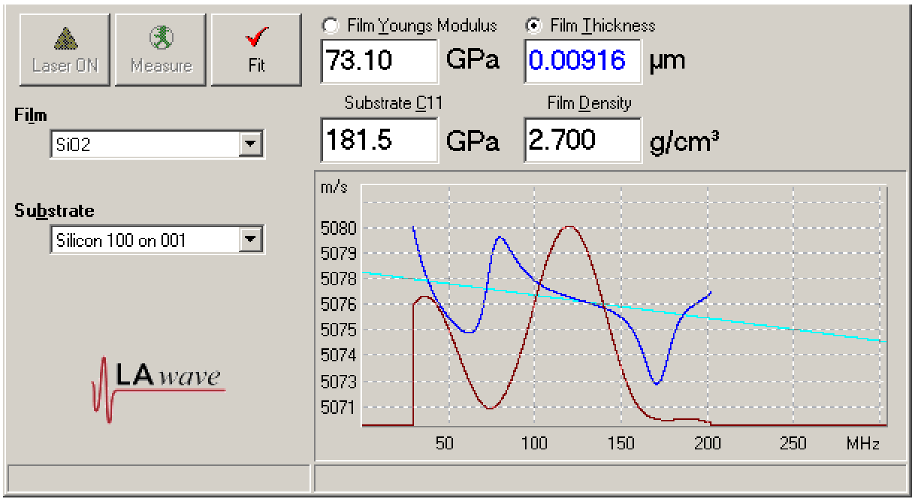
○ Film Youngs Modulus: 73.10 GPa
● Film Thickness: 0.000 µm
Substrate C11: 181.6 GPa
Film Density: 2.700 g/cm³
Film: SiO2
Substrate: Silicon 100 on 001

Figure 3: Young’s modulus determination for natural oxide sample



○ Film Youngs Modulus: 73.10 GPa
● Film Thickness: 0.00512 µm
Substrate C11: 181.7 GPa
Film Density: 2.700 g/cm³
Film: SiO2
Substrate: Silicon 100 on 001

Figure 4: Young’s modulus determination for 5 nm thermal oxide sample



○ Film Youngs Modulus: 73.10 GPa
● Film Thickness: 0.00916 µm
Substrate C11: 181.5 GPa
Film Density: 2.700 g/cm³
Film: SiO2
Substrate: Silicon 100 on 001

Figure 5: Young’s modulus determination for 10 nm thermal oxide sample

## 3.2 SURFACE CHARGE MEASUREMENTS

The accumulation of static change on a silicon artefact which has an oxide overlayer is a major issue when determining the mass of the artefact. The charge accumulation and the effectiveness of three discharging methods was assessed for all the silicon samples.

### 3.2.1 Charge induction

Two methods were used to charge the samples, a spark gun based on a modified gas appliance igniter and a friction method using a nylon sheet. Once charged the level of charge was measured using an AlphaLab SVM2 surface DC voltmeter.

### 3.2.2 Charge removal

The samples were then treated with one of the anti-static methods described below and the level of static charge re-measured. The use of the Zerostat anti-static pistol involved shooting negative ions at the surface of the samples. Three “shots” were used for each treatment. The Fraser ion source was set up in a glove box and the charged samples were left in the glove box for 30 minutes for each charge removal. Treatment with ultra-violet light involved exposing the surface of the samples to UV light in a sealed enclosure for a period of 30 minutes.

The equipment used for the tests is shown in Figures 6 and 7 and the results are given in Table 1.

**Figure 6: AlphaLab Surface DC voltmeter**

**Figure 7: Static charge removal equipment (Zerostat anti-static gun, Fraser ion source, UV lamp)**

**Table 1: results of charging and anti-static treatment on the three silicon samples.**

| Test no. | Device | Treatment | Condition | Measured surface charge / kV | | |
|---|---|---|---|---|---|---|
| | | | | Native oxide | 5 nm thermal oxide | 10 nm thermal oxide |
| | | | | | | |
| 1.1 | | Spark gun | Charged | 0.628 | 0.733 | 0.632 |
| 1.2 | | UV | Discharged | 0.01 | 0.008 | 0.003 |
| 1.3 | | Spark gun | Charged | 0.411 | 0.582 | 0.489 |
| 1.4 | Fraser | ioniser | Discharged | 0.014 | 0.008 | 0.013 |
| 1.5 | | Spark gun | Charged | 0.566 | 0.355 | 0.677 |
| 1.6 | Zerostat | anti-stat gun | Discharged | 0.044 | 0.019 | 0.034 |
| | | | | | | |
| 2.1 | | Friction | Charged | 0.844 | 0.902 | 1.107 |
| 2.2 | | UV | Discharged | 0.008 | 0.007 | 0.011 |
| 2.3 | | Friction | Charged | 0.801 | 0.811 | 0.787 |
| 2.4 | Fraser | ioniser | Discharged | 0.008 | 0.022 | 0.012 |
| 2.5 | | Friction | Charged | 0.882 | 0.791 | 0.918 |
| 2.6 | Zerostat | anti-stat gun | Discharged | 0.032 | 0.041 | 0.054 |
| | | | | | | |
| 3.1 | | Spark gun | Charged | 0.606 | 0.708 | 0.781 |
| 3.2 | | UV | Discharged | 0.009 | 0.011 | 0.012 |
| 3.3 | | Spark gun | Charged | 0.481 | 0.522 | 0.544 |
| 3.4 | Fraser | ioniser | Discharged | 0.031 | 0.019 | 0.012 |
| 3.5 | | Spark gun | Charged | 0.489 | 0.552 | 0.611 |
| 3.6 | Zerostat | anti-stat gun | Discharged | 0.032 | 0.018 | 0.031 |
| | | | | | | |
| 4.1 | | Friction | Charged | 0.89 | 0.778 | 0.919 |
| 4.2 | | UV | Discharged | 0.007 | 0.006 | 0.009 |
| 4.3 | | Friction | Charged | 0.771 | 0.69 | 0.891 |
| 4.4 | Fraser | ioniser | Discharged | 0.022 | 0.023 | 0.012 |
| 4.5 | | Friction | Charged | 0.607 | 0.881 | 0.591 |
| 4.6 | Zerostat | anti-stat gun | Discharged | 0.009 | 0.008 | 0.032 |
| | | | | | | |
| | | Average change / kV | | 0.665 | 0.692 | 0.746 |
| | | Average after UV / kV | | 0.009 | 0.008 | 0.009 |
| | | Average after ioniser / kV | | 0.019 | 0.018 | 0.012 |
| | | Average after anti-stat / kV | | 0.029 | 0.022 | 0.038 |

## 4 DISCUSSION AND CONCLUSIONS

Three samples of silicon were prepared one with a natural oxide layer and two with thermally grown oxides of nominal depth 5 nanometres and 10 nanometres. The aim was to determine and compare the surface hardness and charge accumulation/retention properties of the three samples.

It was not possible to make a determination of the hardness of the surface (oxide) layer of the silicon samples by micro-indentation measurements or using an instrumented indenter due to the thin nature of the oxide layer. Surface acoustic wave measurements were used to assess the hardness of the surface oxide layers assuming the thickness of the oxide layers and the Young's modulus of the substrate. For all three samples the calculated Young's modulus for the oxide layer was 73.1 GPa (comparable with published data for the bulk properties [1] and for surface oxide layers [2,3]). This suggests that with all samples (including the one with only the natural oxide) the oxide depth was sufficient for the surface acoustic wave measurement technique to measure the modulus of the oxide. The relatively low value of Young's modulus also confirms the relative lack of robustness of the (oxide) surface on silicon artefacts and the need for careful handling in order to maintain a stable mas value.

The samples were charged using two different techniques and then treated with three forms of anti-static apparatus to assess the effectiveness of removing the surface static charge. Both forms of charge accumulation successfully induced a significant level of static charge in the samples. There was a small difference between the average levels of charge induced on the three samples with the sample with 10 nm thermal oxide accumulating the highest level of static charge. However, given the repeatability of the charge induction techniques the differences in induced charge are not significant. All three charge dissipation methods proved successful in removing the majority of the induced static charge, with exposure to ultraviolet light (for a period of 30 minutes) being the most successful.

## 5 REFERENCES

[1] Kaye and Laby, Tables of Physical & Chemical Constants, http://www.kayelaby.npl.co.uk/.

[2] Stoichiometry of thin silicon oxide layers on silicon, T. W. Sigmon, W. K. Chu, E. Lugujjo and J. W. Mayer, Appl. Phys. Lett. 24, 1974, 105.

[3] The influence of oxide and adsorbates on the nano-mechanical response of silicon surfaces, S. A. Syed Asifa, K. J. Wahla and R. J. Coltona, Journal of Materials Research, Volume 15, 02, 2000, 546-553.

## ACKNOWLEDGEMENTS

The work leading to the results described in this publication is part of the European Metrology Research Programme (EMRP), which is jointly funded by the EMRP participating countries within the European Association of National Metrology Institutes (EURAMET) and the European Union.