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Anomalous optical surface absorption in nominally pure silicon samples at 1550 nm

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Abstract

The announcement of the direct detection of gravitational waves (GW) by the LIGO and Virgo collaboration in February 2016 has removed any uncertainty around the possibility of GW astronomy. It has demonstrated that future detectors with sensitivities ten times greater than the Advanced LIGO detectors would see thousands of events per year. Many proposals for such future interferometric GW detectors assume the use of silicon test masses. Silicon has low mechanical loss at low temperatures, which leads to low displacement noise for a suspended interferometer mirror. In addition to the low mechanical loss, it is a requirement that the test masses have a low optical loss. Measurements at 1550 nm have indicated that material with a low enough bulk absorption is available; however there have been suggestions that this low absorption material has a surface absorption of >100 ppm which could preclude its use in future cryogenic detectors. We show in this paper that this surface loss is not intrinsic but is likely to be a result of particular polishing techniques and can be removed or avoided by the correct polishing procedure. This is an important step towards high gravitational wave detection rates in silicon based instruments.

Keywords: gravitational wave detectors, optical absorption, silicon optics

(Some figures may appear in colour only in the online journal)

1. Introduction

The direct detection of GW by the two LIGO detectors on the 14 September 2015 [1] opened the new era of GW astronomy. The LIGO detectors will soon be joined by the AdVirgo detector in Italy, as the first steps towards a worldwide network of detectors. These interferometric GW detectors [2, 3] operate by measuring the differential displacement of test masses in the arms of large-scale Michelson interferometers. Reflective coatings on these test masses form the mirrors of Fabry–Perot cavities in the interferometer arms. It is expected that aLIGO and AdVirgo will eventually be limited in their sensitivity in the frequency range around 60 Hz, by the thermal noise associated with the mechanical loss of the reflective coatings on the test masses [4]. Future detectors are likely to operate well below room temperature to avoid this limitation. Proposals for such devices have suggested using silicon test masses, with lasers at 1550 nm for the light sources [5]. Silicon has superior mechanical loss properties to fused silica [6] (which is used in current GW detectors) at low temperatures. There are two temperatures where the thermal expansion coefficient of silicon goes to zero, 120 K and 20 K, which provide minima in thermo-elastic noise [7, 8]. Intrinsically, the optical absorption in pure silicon above 1450 nm is negligible ($<10^{-8}$ cm^{-1}) [9], but impurities can cause absorption directly, or by providing additional free carriers within the material. Recent work [10] has shown that the room temperature bulk optical absorption at 1550 nm of some commercially available material is at a level suitable for its use as a mirror substrate in a GW detector, and further investigations [11] indicate that the cryogenic absorption is similar. Operating at cryogenic temperatures requires control of heat input to the test mass, to keep the mass at the operating temperature. Absorption from the laser beam can become the dominant heat input to the test mass and the removal of this heat can become a limiting factor to operation. One can talk about the allowed heat budget, which is the amount of absorbed power beyond which it would no longer be possible to keep the test mass at the required operating temperature. In the high vacuum environment around a GW detector test mass, one can remove heat from the test mass by conduction or by radiation. Mechanical isolation of the test masses, usually through a multi-stage pendulum, will place limits on the rate of conductive cooling. The suspension elements of the final pendulum stage are the only direct conductive heat path to the test mass. Mechanical isolation usually requires thin, long, suspension elements (fibres or wires). This is diametrically opposed to what one requires for good heat conduction. Without a specific design in mind and therefore a known heat removal rate, it is difficult to put a limit on how much heat input to the test mass is allowed from absorption of the laser beam. However, removing more than a few watts, either by conduction through the suspension elements or by radiation to a lower temperature shield, seems challenging.

The power of radiative cooling drops very quickly with temperature, as determined by the Stefan–Boltzmann law. A perfect black body at 300 K can radiate 450 W m^{-2}, whereas this has dropped to around 10 W m^{-2} at 120 K and 0.005 W m^{-2} at 10 K. We choose these temperatures as they are the intended operating temperatures for a proposed upgrade to the aLIGO interferometers [12], known as Voyager, and for the low frequency part of the Einstein telescope (ET LF) detector [4], a European proposal for a 3rd generation detector. Both these designs use silicon mirror substrates, cryogenically cooled, as test masses. The Voyager design will use radiative cooling to remove excess heat from the test mass, whereas the ET LF design looks to use conduction through the suspension elements.

In the Voyager design it is envisioned that there will be a laser power of several kilowatts in the substrate of the input test mass. This means a surface absorption of order 100 ppm would dump close to one watt from the laser into the test mass. This would be a significant fraction of the total allowable heat budget for the input test mass, as the test mass surface area will be

approximately 1 m^2. Ensuring that surface absorption will be significantly less than this value would mitigate against any problems in this part of the system design.

The ET LF design assumes an absorption of order 1 ppm of the laser beam in the reflective coating of the arm cavity mirrors. The 18 kW arm cavity power and 1 ppm absorption gives a laser heating of 18 mW. In the design study, this is the only heating of the substrate by the laser. The arm cavity parameters in the ET LF design study imply that there is 33 W of optical power in the substrate of the input test mass. If there was a 100 ppm surface absorption in that optic, it would produce 6.6 mW of excess heating per surface of the input test mass, unaccounted for in the design. This is significant compared to the total heating expected in the ET LF design. It is therefore important to understand where any excess surface absorption originates and how it can be reduced or removed.

The rest of this paper describes our work on understanding the surface absorption measured in some samples tested at the Institute for Gravitational Research. In section 2 we introduce the initial observations of surface absorption. In section 3 we discuss the techniques used to measure the absorption and in section 4 we give details of that absorption. In section 5 we look at various methods used to remove the source of absorption, in 6 we confirm the absorbing species for one polishing method, and in 7 we summarise the our observations and provide our conclusions.

2. Motivation

As part of a study of the optical absorption at 1550 nm of very pure silicon samples, we observed that a number of samples showed absorption features at the surface or surfaces. Although this observation was not universal to all samples, it was common and was seen in samples from different vendors. It had also been reported elsewhere [13] that high purity samples might have significantly higher surface absorption than expected. This was something that had not been reported in similar studies of fused silica substrates undertaken in the visible or near infrared region.

Routine cleaning of the samples with organic solvents (acetone, methanol and isopropanol) or First Contact™ [4] did not reduce the level of absorption. The various samples used in this study are listed in table 1, along with the information known about each one. The samples came from four different vendors, and all but one were nominally pure with resistivity greater than 10 k$\Omega \cdot$ cm. These were produced by the floatzone process. One sample (AEI35) with a lower purity produced by Czochralski growth was also included. Both (1 0 0) and (1 1 1) orientated samples were measured and all samples had optically polished surfaces with a surface flatness of 150 nm or better. The next section describes the techniques used to measure optical absorption at the 1–100 ppm level.

3. Measurement techniques

The initial measurements in this study on bulk and surface absorption were made using a photothermal common-path interferometer (PCI) [14]. In this technique, a pump beam at the wavelength of interest is focussed within a larger probe beam, inside a sample. The interferometric nature of this technique makes it very sensitive, and the common path nature means many noise sources are rejected. With a 10 W pump source, one can readily measure absorptions at or below the 1 ppm level in many optical materials. While using this technique, we noticed that some samples, e.g. AEI35, had surface features with losses of >100 ppm.

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[4] FirstContact™ is a proprietary polymer coating used to clean optical surfaces.

Table 1. Sample identification, known properties and measured absorption. All samples are 25 mm diameter cylinders with polished end faces. The absorption values are typical values, determined from several measurements of each sample.

Sample	Vendor	Orientation	Length (mm)	Flatness or roughness	Resistivity kΩ cm	Bulk absorption (ppm cm^{-1})	Surface absorption (ppm) S1, S2
Floatzone grown							
ALK1	Alkor	(1 1 1)	10	<65 nm	>50	25	5, 34
ALK2	Alkor	(1 1 1)	20	<65 nm	>50	30	12, 460
AEI32	Topsil	(1 0 0)	32	Superpolish (0.3 nm rms)	30–70	<10	14, 36
AEI98	Topsil	(1 0 0)	98	Superpolish (0.3 nm rms)	30–70	20	14, 50
CRY1	Crystran	(1 1 1)	10	<150 nm	>10	17	<1, <1
Czochralski grown							
AEI35	Matek	(1 0 0)	35	<65 nm	~0.5	250	36, 230
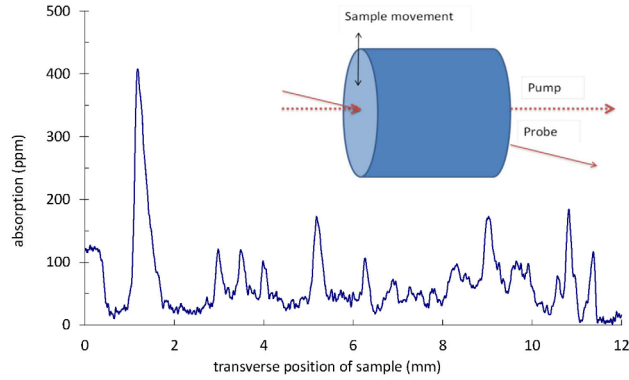
Figure 1. Absorption measurement along a line across the surface of sample AEI 35. The peaks in the absorption, which have a width consistent with the 70 μm diameter of the pump beam, sit on top of a background of around 50 ppm.

The transverse resolution of this technique is given by the pump beam diameter, ~70 μm in our set-up. By scanning the sample transverse to the propagation direction of the pump beam, we were able to look at the variation in absorption across the surface. The results of such a scan are shown in figure 1. There appeared to be large variations in absorption, and the higher absorption regions had transverse dimensions consistent with the resolution limit.

The PCI technique measures absorption using the change in refractive index caused by the material response to changes in temperature, due to absorption of the pump beam. In semiconductors, in addition to the intra-band absorption that directly heats the material, there is also the possibility of creating free carrier pairs through inter-band absorption. This occurs when transitions are excited across the semiconductor bandgap, creating free electron–hole pairs. These free carriers can interact with the probe beam directly, through absorption and refraction [15], as well as indirectly, through further absorption of the pump light. The refractive index changes caused by free carrier density changes can be very much stronger than those caused by the temperature change from the heat deposited by 2-photon absorption. As mentioned earlier, at 1550 nm in silicon, the single photon transition rate across the bandgap is negligible, but the 2-photon rate, which is intensity dependent, may not be. The 2-photon absorption coefficient, β, is 4.5×10^{-12} m W^{-1}, which means for our implementation of the

PCI with a 70 micron diameter pump beam and 1 W power, the absorption due to 2-photon transitions is 100 ppm cm^{-1}. As mentioned above, the dominant effect from this is the signal due to the free carriers created, rather than the direct heating due to the absorption.

To reduce the 2-photon effects with respect to any linear absorption, we can increase the pump diameter to reduce the intensity. In our case, we found it was necessary to increase the beam diameter to around 1 mm to ensure that non-linear effects were less than the linear contribution at a pump power of 1 W. The PCI technique makes use of a property of Gaussian beams: when a Gaussian beam is focussed to a waist, the beam acquires an additional 180° of phase traversing the focussed region compared to one that has not been focused. The distance the beam must travel to acquire this extra phase is proportional to the square of the beam diameter at the waist. Using larger beams will therefore greatly increase the size of the apparatus and, it is more convenient to move away from the PCI technique and use the photothermal deflection (PD) technique [16] when working with ~1 mm diameter pump beams. The larger beams reduce the spatial resolution of the measurements, but enable us to measure down to much lower absorption levels before being dominated by nonlinear effects. For this reason, after the initial work on the AEI35 sample which has a relatively high value of linear bulk absorption, most of the investigation was carried out using PD.

The PD technique relies on the deflection of a probe beam by the refractive index profile induced in a material by absorption of a pump beam. The spatial resolution of PD along the beam direction is given by $w/\sin\gamma$, where w is the pump beam $1/e^2$ radius and γ is the angle between pump and probe beam. For the measurements described in this paper, we had a longitudinal resolution of 5–7 mm, enabling us to just resolve the surfaces of 10 mm thick samples. The transverse resolution is reduced from the PCI case to approximately 1 mm, due to the larger pump beam radius.

4. Details of absorption

The level of surface absorption measured on each sample was not constant across the surface, but each sample seemed to have a minimum absorption level, which was observed at several positions. Transverse to the beam direction, the resolution is determined by the pump beam diameter. In the case of all the PD measurements presented here, the transverse resolution was 1.2 mm. In the case of the single PCI measurement presented it was 70 μm.

The variation in absorption from position to position was as much as a factor of 3 (see for example figure 3). There was some evidence that this variation was reduced after the multiple etching stages described in the next section, without affecting the minimum absorption. The following part of the paper describes how etching was used to remove small amounts of material from the sample surfaces to try and determine the location of the absorption.

5. Removal of surface absorption

5.1. Oxide etch

There had been suggestions that an oxide layer, either silicon dioxide (SiO_2) or silicon monoxide (SiO) on the surface of the silicon could cause absorption. Ellipsometry measurements of sample AEI35 were best fitted by a 2.5 nm layer of SiO_2. This is what one would expect, and is often referred to as the 'native oxide' layer (produced by reaction between the silicon and atmospheric oxygen), but we felt it was important to rule out this layer as being an issue. The first step in our investigation was to perform an etch with buffered hydrofluoric (HF) acid solution. The etch rates of SiO and SiO_2 are well characterised [17]. We exposed two samples (AEI32 and AEI98) to the etch solution for 5 min, long enough to remove the equivalent

of several nanometers of SiO, or tens of nanometers of SiO_2. The sample absorption was measured within a few hours of etching, to ensure that minimal oxide regrowth would have occurred [18]. No significant reduction in absorption was measured after this etch process.

5.2. Silicon etch

Given that the absorption was not present in the oxide layer, it must lie within the silicon itself. There could be several hypotheses on what was causing the absorption, and one way to help choose between them would be to ascertain at what depth within the crystal the absorption was taking place. As our technique did not have the resolution to do this directly, we used further etching processes to obtain the information. Two possibilities were considered:

 (1) amorphous silicon forming a layer or series of small islands on the surface due to mechanical effects during polishing [13];
 (2) contamination due to material used during the polishing process becoming trapped within the surface.

It was expected that any amorphous silicon would be on or very close to the surface, whereas any material implanted during the polishing process could lie at a depth related to the flatness specification of the surface. During polishing, material is removed from high points on the surface and can accumulate in valleys, and so the depth at which the absorption takes place would depend on the surface roughness of the material at that point in the process.

Subsequently, we decided to carry out a two stage etch process on samples AEI32 and AEI98: the first stage to remove around 5 nm of silicon and look for influence of amorphous surface material or material deposited at the end of the polishing process; the second stage to remove up to 100 nm of silicon and look for influence of material deposited earlier in the polishing process. Both surfaces of the AEI32 sample were etched, whereas only a single surface of the longer AEI98 sample was etched.

These etch stages were undertaken with 30% KOH solution at 50 °C. The desired etch depths were calculated and a resist was used to mask off part of the sample, to allow a measurement of the actual material removed.

In the first etch, removal of 5 nm of material showed no change in absorption.

In the 2nd etch, 80 nm of material was removed, as measured using a Wyko surface profiler (see figure 2). The absorption was measured using the PD technique, scanning the crossing point of the pump and probe beam through the sample. The longitudinal resolution (as can be seen in figure 3) is about 8 mm, whereas the transverse resolution is about 1 mm. The different coloured traces refer to different transverse positions on the sample. One surface of the sample absorbs significantly more than the other, and this was true both before and after etching. The variability in absorption from place to place on the surface of the sample was much greater than any systematic difference caused by etching. It seems that the surface absorption was only minimally affected by the etch process.

5.3. Mechanical polish

After the chemical etch processes, we investigated the effect of mechanical removal of surface material. We sent all the samples in table 1, except AEI35, to have one surface polished. The polishing was carried out by Crystran[5], as their samples, when originally supplied, showed no sign of surface absorption. We asked the company to repolish the samples' surfaces with

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[5] Crystran Ltd, 1 Broom Road Business Park, Poole, Dorset BH12 4PA, UK.
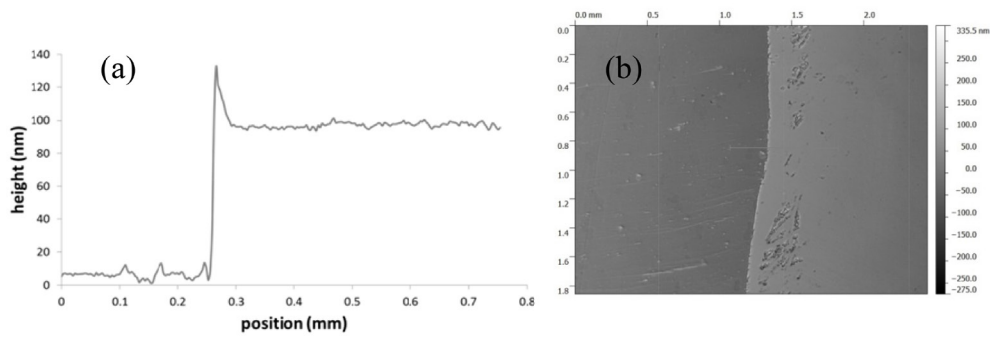
Figure 2. Etched sample (AEI32) (using a Wyko NT1100 optical surface profiler) after the photoresist was removed. (a) line scan across the step at 0.27 mm between the area unprotected during the etch and the area covered with photoresist, (b) grey scale surface profile of same sample.
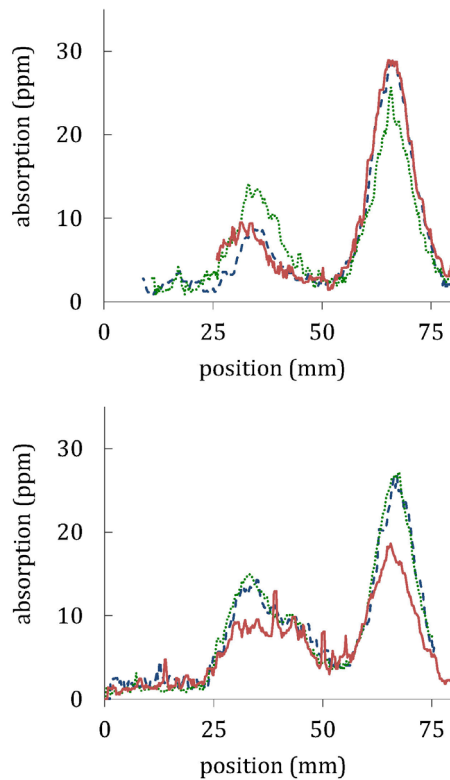
Figure 3. Longitudinal absorption scans of the AEI32 sample made before (top) and after (bottom) the 80 nm KOH etch. The different traces correspond to different transverse positions. These transverse positions are **not** the same in the two panels.
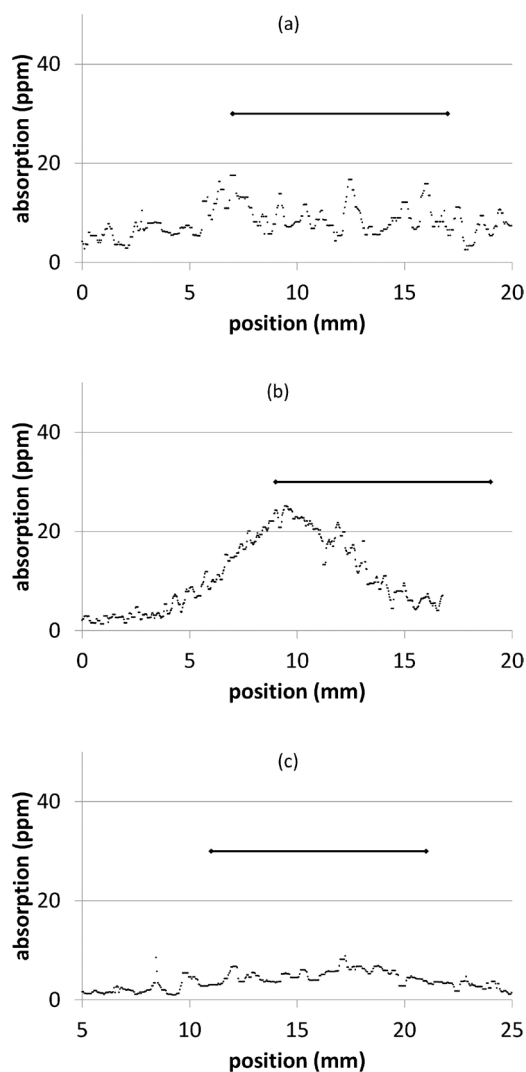
Figure 4. Sample CRY1 measured as delivered (a), after Bindzyl polish (b), and after polishing with Nalco (c). In each panel, the black horizontal bar represents the position of the sample. The noise in panel (a) is higher due to a shorter averaging time.

the minimal removal of material and so they used a process different to what they normally would do. They used a Bindzil[6] slurry to do a final stage polish (removing only a few microns of material) without the preparatory steps that would require much more material removal.

After this polish, the samples were returned for absorption measurement. All samples showed an increase in surface absorption, this included one sample, CRY1, that had shown no previous surface absorption; see figure 4(a). This was the first time we had been able to systematically change the surface absorption, by which we mean that all the samples had their surface absorption altered to the same value by polishing.

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[6] The trade names of 'Nalco' and 'Bindzyl' refer to somewhat generic polishing slurries and are not specific enough to describe the conditions fully. They do however identify the main polishing component as colloidal silica for both.
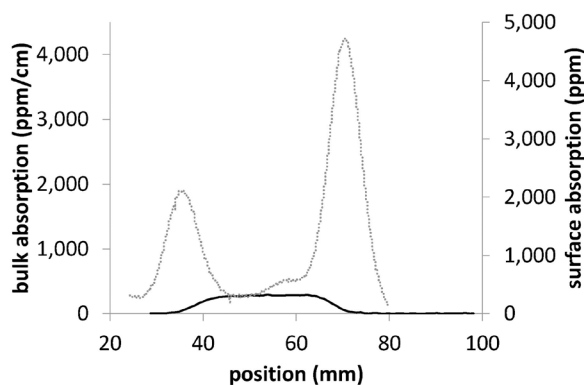
Figure 5. Czochralski grown sample AEI35. The graph shows measurements taken after the sample was polished at both ends using diamond grit (grey dotted line) and then colloidal silica 'Nalco' (black line). The left hand scale calibrates the signal for bulk absorption, the right hand for surface absorption.

However, our aim was to remove the surface absorption rather than equalise it, and so we returned two of the samples (CRY1 and ALK1) to the vendor for a second polish, this time of both surfaces of the samples. This polish was carried out using Crystran's standard procedure; the samples were initially ground, removing of order one hundred microns of material, before being polished with a Nalco slurry. The absorption measurements from this second polish provided completely different results, as can be seen in figure 4. Figure 4 shows sample CRY1 measured: (a) as originally delivered; (b) after the 'Bindzyl polish'; (c) after the 'Nalco polish'. The longitudinal spatial resolution calculated from the beam size and crossing angle is 8 mm which matches the width of the signal seen from the single absorbing surface in (b). The surface absorption that was seen in (b) has disappeared in (c), and all that can be seen is the absorption of the bulk material. From this, it is clear that the first polishing method was creating a surface absorption effect and the second process has then removed it.

6. Identification of absorbing species for one polishing method

It was of interest whether the purity of the material had an effect on the level of surface absorption after polishing. All the samples measured in the discussion above were float zone grown material with a resistivity of greater than $10 \, k\Omega \cdot cm$. To investigate the effect of resistivity on surface absorption, we had the sample of Czochralski grown material (AEI35) polished. This material had a resistivity of $500 \, \Omega \cdot cm$ and had been previously measured to show surface absorption of 36 ppm and 230 ppm for its two surfaces, and have a bulk absorption of 250 ppm cm^{-1}. To remove this 'as delivered' surface absorption, we intended to have this sample polished with a Nalco slurry. However, owing to a misunderstanding with the polishing company, the sample was actually polished with diamond grit. After this polish, the sample showed a very high level of surface absorption at 1550 nm—over 3000 ppm on one surface, as is shown in figure 5. X-ray fluorescence analysis of the surfaces showed that germanium (Ge) was present at a level of a few tens of parts per million. This is near the limit of the sensitivity of our particular equipment. Ge in silicon is known to have a high absorption at 1550 nm [19].

The sample was then returned to the polisher, and this time polished with Nalco. Subsequently measurement showed no indication of any surface absorption and x-ray fluorescence did not show any Ge at the surface. It seems clear that in this case the surface

absorption was caused directly by contamination due to Ge in the polishing method. However, for that polishing method, the levels of absorption in this sample were particularly high, which allowed the positive identification of the contaminant. For the other polishing methods that showed the lower surface absorption this was not the case. For these lower absorbing surfaces it may be that contaminants are present at too low a level to detect with our x-ray fluorescence equipment, or it may be that the absorption is as a result of different surface chemistry in these samples.

7. Summary and conclusions

The work in this paper shows that reports of excess surface absorption in silicon are not due to an intrinsic absorption of the material. From our various measurements we show that, depending on the polishing method, or surface treatment, one can induce a surface absorption in silicon at a level significantly above that produced by the bulk in pure samples. We show that one can avoid this excess absorption by treating the surface with the correct method. In this paper, we have shown that the absorption is not due to the native oxide layer and that one cannot remove the excess absorption by etching away up to 100 nm of the surface material. We have shown that repolishing of the surface with the correct technique will completely remove the excess absorption. It is interesting to speculate whether the absorption is caused by material within the surface, or by the chemistry of the surface layer. Further experiments are planned to look systematically at how the surface absorption produced by polishing depends on slurry compound, polishing pad and pH level.

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