

Silicon Lattice Comparisons Related to the Avogadro Project: Uniformity of New Material and Surface Preparation Effects

Ernest G. Kessler Jr., Scott M. Owens, Albert Henins, and Richard D. Deslattes

Abstract— New high-quality silicon has been produced by Wacker Siltronic¹ as potential starting material for a precision determination of the Avogadro constant, N_A . An assessment of the uniformity of this material is an essential first step in determining whether this material is of sufficient quality to be used in this project. We have made extensive measurements to determine lattice parameter uniformity of several regions of this new material using the NIST lattice comparator. Measurements from this comparator have been shown to have a relative internal consistency near 1×10^{-8} . In the course of these measurements we noted a significant dependence of lattice parameter values on surface preparation of the samples. Samples prepared by grinding followed by chemical-mechanical (c-m) polishing show a wider distribution than samples prepared by grinding followed by etching. Surface preparation procedures were altered to include etching after c-m polishing. This unexpected dependence on surface preparation raises the possibility that some of the NIST lattice comparison results presented at CPEM96 may be biased by surface preparation effects. To test this possibility, some of the samples included in our CPEM96 contribution have been etched and remeasured. Preliminary estimates of corrections to some NIST CPEM96 lattice comparison results appear to confirm that bias.

Index Terms— Avogadro constant, crystal lattice comparison, silicon, surface preparation, X-ray diffraction, X-ray measurements.

I. THE NIST LATTICE COMPARATOR

THE lattice parameter uniformity study of the new silicon material was carried out using the NIST lattice spacing comparator. This instrument measures the changes in Bragg angle, θ , between different crystal samples and uses the differential form of the Bragg equation, $\Delta d/d = -\cot \theta (\Delta \theta)$, to infer changes in the lattice spacing, d . The comparator is a two crystal diffractometer that has two X-ray tubes, two detectors, and a translation device for automatic interchange of crystal samples which are used in the second crystal position. All profiles are recorded using a nearly nondispersive geometry which is insensitive to the spread in wavelength, $\Delta \lambda$, of the X-ray line. Changes in Bragg angle are measured using a heterodyne angle interferometer, which is calibrated with an optical polygon. Sensitivity to drifts is minimized

¹The use of the company name Wacker Siltronic is included to identify the silicon supplier. Such identification does not suggest endorsement.

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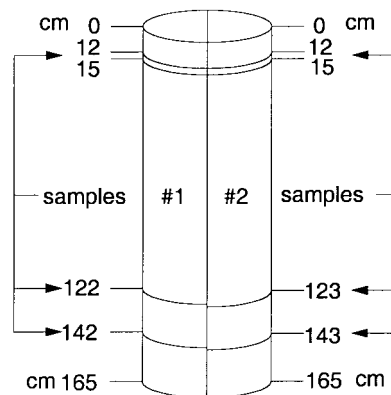


Fig. 1. Location of lattice comparison samples in new Si material. Ingot #1: no nitrogen doping; ingot #2: nitrogen doped.

by simultaneous recording of X-ray profiles. The crystals are prepared with nearly equal thicknesses ($\pm 3 \mu\text{m}$) in order that the profiles have pronounced pendellösung oscillations which significantly increase (≈ 50) the pointing precision of the X-ray profiles. The total relative uncertainty of the lattice comparator measurements is about 1×10^{-8} . A more complete description of the NIST lattice comparator can be found in [1].

II. UNIFORMITY MEASUREMENTS OF THE NEW SILICON MATERIAL RELATED TO THE AVOGADRO PROJECT

Two ingots of hyperpure float-zoned silicon crystals were produced by Wacker Siltronic specifically for research projects related to an improved determination of the Avogadro constant [2]. The ingots are approximately 165 cm long and 100 mm in diameter. One of the ingots was grown with a slight nitrogen doping to prevent the agglomeration of self-point defects to swirl defects. NIST was supplied with 3 cm thick samples from the 12 cm to 15 cm regions and with 20 cm thick samples from the 120 cm to 140 cm regions of each of the ingots. Fig. 1 shows the positions of the samples that were used for uniformity measurements at NIST. The measurement positions for the crystal samples taken from the 120 cm to 140 cm regions were approximately along a diameter, while the measurement positions from the crystal samples taken from the 12 cm to 15 cm regions were on a chord about 20 mm from the center. Radial and longitudinal variations of lattice parameter uniformity were measured for

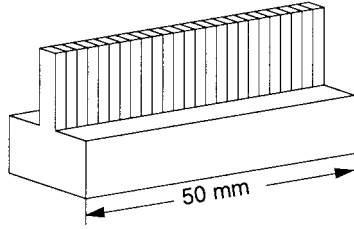


Fig. 2. Drawing of the crystal samples cut from the new Si material. The thin blade is taken from a disk normal to the longitudinal axis of the ingot.

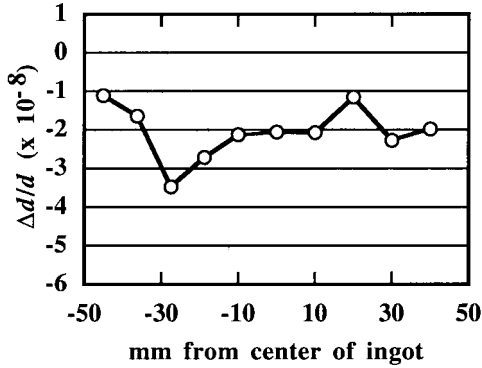


Fig. 3. Radial variation $\Delta d/d$ of the lattice parameter for one longitudinal position using samples prepared by grinding and etching. The relative uncertainty for each data point is $\approx 1 \times 10^{-8}$.

all of the samples. Because the lattice comparator can not accommodate 100 mm long samples, two samples, one about 55 mm long and a second about 45 mm long, were used to traverse each diameter or chord. A drawing of a typical crystal sample appropriate for the NIST lattice comparator is shown in Fig. 2. The crystals are used in transmission and the diffraction occurs at the thin blade. The thick base is waxed to a single central support to provide a strain free mounting. The initial samples were prepared by grinding followed by etching to remove surface damage. Approximately $30 \mu\text{m}$ of material was removed by etching from each surface. For all of the measurements reported here, the standard crystal was a sample of WASO17 supplied by PTB and prepared at NIST. The results are reported as the unknown—the standard (WASO17). Fig. 3 shows the spatial variation of the lattice parameter for one longitudinal position. In total, more than 100 lattice parameter comparisons were performed on samples from the two ingots. From the data we draw the following conclusions:

- 1) the average lattice parameter of the two ingots is the same to within one part in 10^8 of the measured d value;
- 2) no significant radial or longitudinal variation in lattice parameter was noted in either ingot;
- 3) the average lattice parameter of the new silicon material is approximately 2×10^{-8} smaller than the NIST sample of WASO17.

A histogram of all of the measurements is presented in Fig. 4 and shows a full width at half maximum $< 2 \times 10^{-8}$, which we take as a reasonable estimate of the uniformity of this Si material.

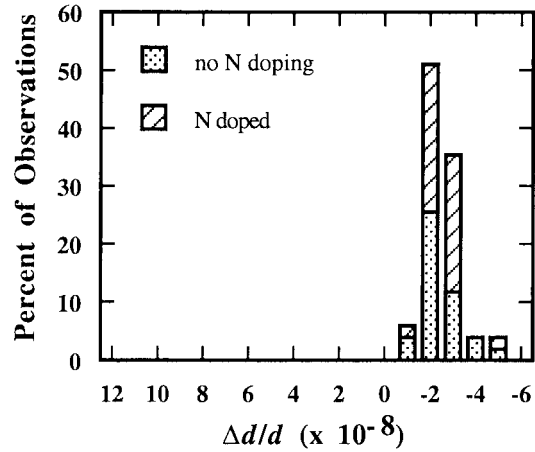


Fig. 4. Histogram showing the variation of the $\Delta d/d$ measurements of the new Si material. All crystal samples were prepared by grinding and etching.

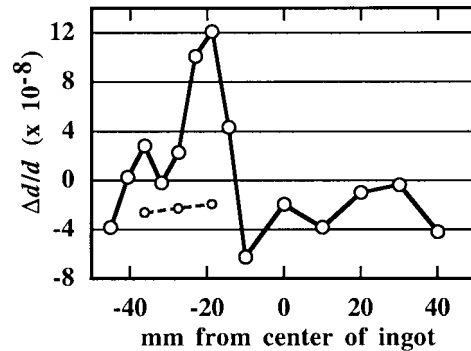


Fig. 5. Radial variation $\Delta d/d$ of the lattice parameter for one longitudinal position using sample prepared by grinding and c-m polishing. $\Delta d/d$ after additional light etching is indicated by the dashed line. The uncertainty for each data point is $\approx 1 \times 10^{-8}$.

III. CRYSTAL SURFACE PREPARATION STUDIES

In addition to $\Delta d/d$ measurements of the new Si material using etched samples, measurements were made using chemical-mechanical (c-m) polished samples. As mentioned above, polishing techniques have been developed to prepare crystals which have nearly equal thicknesses. After grinding, the thin blade of the crystal was c-m polished using a colloidal silica solution. The polishing rate is approximately $10 \mu\text{m/h}$. The polished samples were cut from Si material directly adjacent to that used for the etched samples. The measurement position for the polished samples was along a chord parallel to and approximately 20 mm from the diameter used for the etched samples. Lattice parameter measurements of the polished crystals as a function of radial position show significantly larger variations than measurements of crystals that were only etched. In Fig. 5, we show the measured variation in lattice parameter along a diameter for a polished crystal, which shows a variation larger than 1×10^{-7} over a 30 mm radial distance. Further evidence that the polished samples are troubled by surface preparation effects was provided by lightly etching ($\approx 2 \mu\text{m}$ removed per surface) some of the polished samples, which significantly reduced or eliminated the large variations

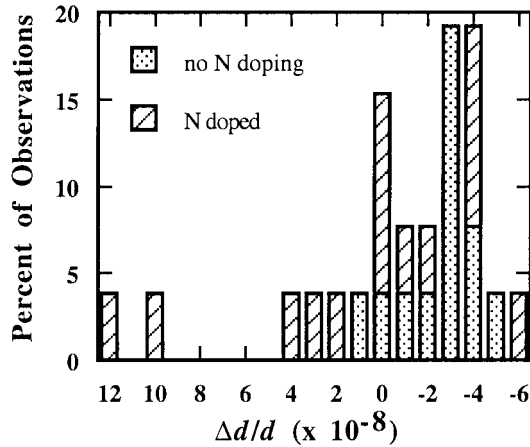


Fig. 6. Histogram showing the variation of the $\Delta d/d$ measurements of the new Si material. All crystal samples were prepared by grinding and chemical-mechanical polishing.

as is indicated by the dashed line in Fig. 5. A histogram of the lattice parameter measurements of the polished Wacker samples is shown in Fig. 6. Comparison of Figs. 4 and 6 leads to the conclusion that the NIST c-m polishing procedure has the potential to bias lattice comparison results.

The large variation in $\Delta d/d$ caused by c-m polishing led us to investigate a third crystal surface preparation procedure. Smaller 20 mm long crystals were cut from the new Si material so that the measurement positions were again along a diameter. After grinding, about 30 μm of material was removed by etching from all of the crystals. The thin blades of some of the crystals were c-m polished flat which removed about 25 μm of additional material. The polished crystals were then etched; some lightly ($\approx 4 \mu\text{m}$ removed) and some more heavily ($\approx 15 \mu\text{m}$ removed). $\Delta d/d$ measurements were made on the three groups of crystals: etched only; etched, c-m polished, lightly etched; and etched, c-m polished, heavily etched. Although we have only measured Si samples from two diameters using this procedure, no significant $\Delta d/d$ variations were noted between these three groups. As noted above, the etching after c-m polishing appears to remove the large variations that polishing can introduce.

IV. THE PTB-NIST LATTICE COMPARISON DISCREPANCY

The NIST lattice comparison measurements that were reported at CPEM96 were made using crystal samples that were c-m polished [2]. Our experience with polished samples from the new Wacker material suggested that these measurements should be reexamined for potential surface preparation bias. We remind the reader that lattice comparison measurements made at PTB and NIST on five different silicon ingots showed that on the average the NIST lattice comparison measurements were smaller than the PTB lattice comparison measurements by $(6.4 \pm 1.5) \times 10^{-8}$. Although the NIST and PTB comparisons used different samples from the same ingots and the NIST standard was WASO17 and the PTB standard was WASO REF, this large difference has caused considerable con-

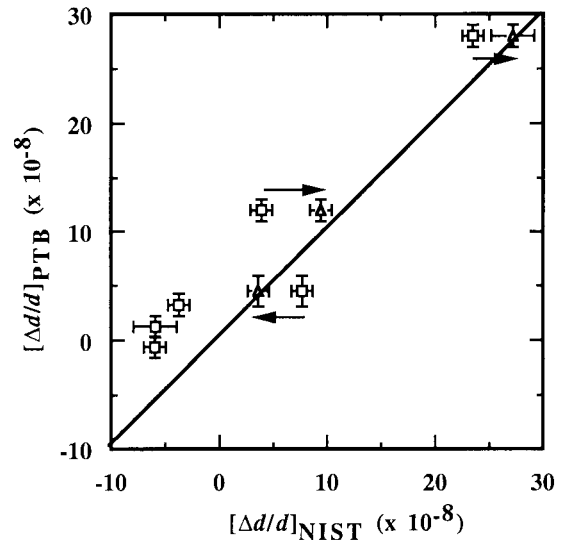


Fig. 7. Comparison of relative measurements at PTB and at NIST. The squares are results presented at CPEM96 and the triangles are estimated from preliminary 1998 measurements. The arrows indicate how the NIST results changed between CPEM96 and CPEM98. Perfectly consistent PTB and NIST measurements would lie on the diagonal line.

cern. A second WASO17 sample (WASO17-2) was prepared at NIST by grinding and etching only. This sample was compared to the original WASO17 sample (WASO17-1), which had been ground and c-m polished. Although these crystals are less than 10 mm wide, measurements were recorded along the central 6 mm to detect any large $\Delta d/d$ variations. The WASO17-1 sample was uniform to within 1×10^{-8} from the central region to one end, but showed larger variation (8×10^{-8}) at the other end. The central region of the WASO17-1 sample, which was used as the NIST WASO17 standard, was larger than the WASO17-2 by 1×10^{-8} . The WASO17-2 sample was uniform to within 1×10^{-8} over the entire central 6 mm region. Light etching (2 μm removed) of the WASO17-1 sample produced a WASO17-1 crystal whose lattice spacing is uniform to within 1×10^{-8} over the central 6 mm region and larger than the WASO17-2 sample by 1×10^{-8} . Recently, another WASO17 sample (WASO17-3) that was prepared at PTB was provided to NIST. Preliminary comparisons of this sample, which is about 35 mm long, to the WASO17-1 sample show a lattice spacing difference $< 1 \times 10^{-8}$. From these measurements on three WASO17 samples we conclude that the WASO17-1 sample (that has been and is currently being used as a standard on the NIST comparator) is representative of the WASO17 silicon to within 1×10^{-8} and is not the cause of the 6.4×10^{-8} discrepancy between the PTB and NIST lattice spacing comparisons [2].

In an attempt at resolving the discrepancy between the PTB and NIST lattice spacing comparisons, we have begun to make additional measurements on samples from three other silicon ingots that were also measured at PTB. Using the designations given in [2, Table I], these samples are IMGC-MO, NRLM-FZ, and PTB/ILL-NCOM. In Fig. 7, we compare the PTB relative measurements to the NIST relative measurements for

all samples that have been measured at both PTB and NIST. The input data for this figure is given in Tables III and IV of [2], except for the PTB measurement of the NRLM-FZ material, which is given in [3]. All of the original NIST samples were c-m polished and no allowance was made for potential surface preparation bias. The additional measurements include remeasurement of the crystal samples used in the CPEM96 report with no modification (c-m polishing only) and with additional etching to remove $2\text{ }\mu\text{m}$ to $4\text{ }\mu\text{m}$ per surface. Our measurements are too preliminary at this time to present numerical results, but we do include three additional points in Fig. 7, which suggest our current best estimate of the relative NIST measurements for these three points. The discrepancy between the PTB and the NIST lattice comparisons appears to be significantly reduced, but still outside the uncertainty of the comparison instruments in some cases. Most of the reduction of the discrepancy is related to surface preparation effects. We incorrectly assumed that the bulk lattice parameter would not be affected by c-m polishing the surface. In addition to the surface preparation, we have reanalyzed the data used in the CPEM96 report and found that the crystal temperature measurements for some of the crystals were incorrect. The published numerical results for the MO and NCOM samples should be increased by about 3×10^{-8} . Thus, part of the discrepancy for some of the crystals can be explained by temperature measurement errors.

V. CONCLUSIONS AND OUTLOOK

Lattice comparison measurements on three regions of the new Avogadro project Si material show that this material is uniform to within about 2×10^{-8} . Preparation of samples for lattice comparison which involves c-m polishing has the potential to produce samples that give erroneous $\Delta d/d$ measurements. Part of the PTB-NIST lattice comparison discrepancy reported at CPEM96 is due to the crystal sample preparation techniques that were used at NIST.

Efforts are underway to improve the NIST lattice comparison capability so that relative uncertainties near 5×10^{-9} will be routine. Interchange of samples between PTB and NIST has begun so that the agreement of $\Delta d/d$ measurements made at these two institutions can be assured.

REFERENCES

- [1] E. G. Kessler, Jr., A. Henins, R. D. Deslattes, L. Nielsen, and M. Arif, "Precision comparison of the lattice parameters of silicon monocrystals," *J. Res. Nat. Inst. Stand. Technol.*, vol. 99, pp. 1-18, 1994.
- [2] E. G. Kessler Jr., J. E. Schweppe, and R. D. Deslattes, "Intercomparison of silicon samples from the Avogadro projects," *IEEE Trans. Instrum. Meas.*, vol. 46, pp. 551-555, 1997.
- [3] J. Martin, U. Kuetgens, J. Stümpel, and P. Becker, private communication.



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