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ABSOLUTE VOLUME MEASRUMENET OF SILICON SPHERES AT NMIJ

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Abstract: The method and devices for absolute volume measurements of 1 kg silicon spheres are described. An interferometer equipped with a direct optical frequency tuning system is used to measure the sphere volume, in which the optical frequency of a diode laser can be tuned continuously over a frequency range of 19 GHz. Accurate frequency changes in the laser produced by this system are used to measure the sphere diameters by phase-shifting interferometry. A total of seventy diameters, which are distributed near-uniformly over the surface of the sphere, are measured in vacuum. The volume of the sphere is determined by fitting the diameters to a series of spherical harmonics. The mass of the sphere is compared with that of the national prototype of the kilogram through a secondary 1 kg standard. The relative combined standard uncertainty in the density determined by direct measurements of the mass and volume is presently estimated to be 7.3×10^{-8}. Recent results on the volume determination for three 1 kg silicon spheres are shown.

Keywords: volume standard, density standard, silicon sphere, Avogadro constant.

1. INTRODUCTION

A density standard based on a single crystal silicon sphere has recently been developed at national metrology institutes [1-4], where the mass of the 1 kg silicon sphere is compared with that of a mass standard traceable to the prototype of the kilogram, and the volume is determined directly by measuring its diameter using an optical interferometer, so that the unit of the density is directly traceable to the SI units of mass and length [5]. The uncertainty in the absolute density determination for silicon spheres is now much smaller than that for other density standards such as water and Zerodure cubes. Silicon spheres are therefore currently being used at many national metrology institutes (NMIs) as a primary density standard.

Since the absolute volume determination is the dominant uncertainty source for the density determination, optical interferometers for silicon spheres have been developed by some of NMIs to reduce the uncertainty in measuring the diameter of the silicon spheres. A scanning-type interferometer for the diameter measurement has been developed at the National Metrology Institute of Japan (NMIJ) [6]. The density of a silicon sphere was determined with a relative uncertainty of 7×10^{-8} [7]. However, a more accurate density determination is strongly required for both the determination of the Avogadro constant by the x-ray crystal density (XRCD) method and the redefinition of the kilogram [8]. For this purpose, an optical interferometer equipped with a direct optical frequency tuning system has been developed at NMIJ [9,10]. The diameters of a silicon sphere were preliminary measured from thirty directions.

In the present work, the number of measurement directions was increased to seventy for a more accurate volume determination. Details on the design of the measurement system and the uncertainty in the volume measurement are described. Recent results of the volume determination for 1 kg silicon spheres are also presented.

2. OPTICAL INTERFEROMETER

Figure 1 shows a schematic drawing of the optical interferometer to determine the diameter of silicon spheres with optical frequency tuning [9,10]. A silicon sphere is placed in a fused-quartz Fabry-Perot etalon. A laser beam from an external cavity diode laser is split into two beams, labeled beam 1 and beam 2, which are reflected by mirrors toward opposite sides of the etalon. Light beams reflected from the inner surface of the etalon plate and the adjacent surface of the sphere interfere to produce concentric circular fringes. These are projected onto CCD cameras (CCD 1 and CCD 2). Measurements of the fractional fringe order of interference for the gaps between the sphere and the etalon, d_1 and d_2, are made by phase-shifting interferometry. This method requires 6 successive optical frequency changes.

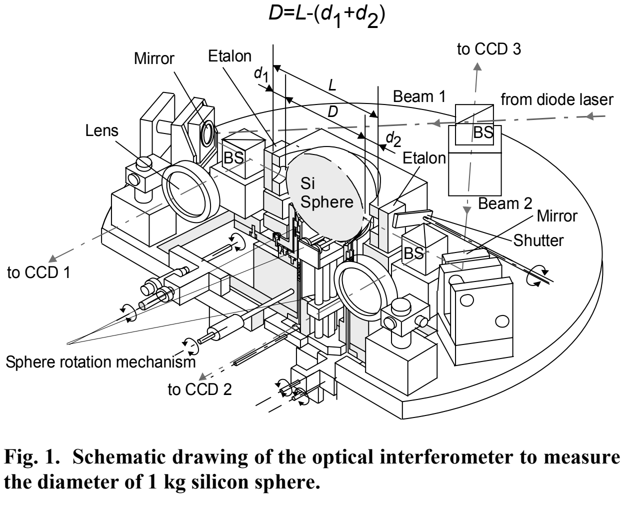

Fig. 1. Schematic drawing of the optical interferometer to measure the diameter of 1 kg silicon sphere.

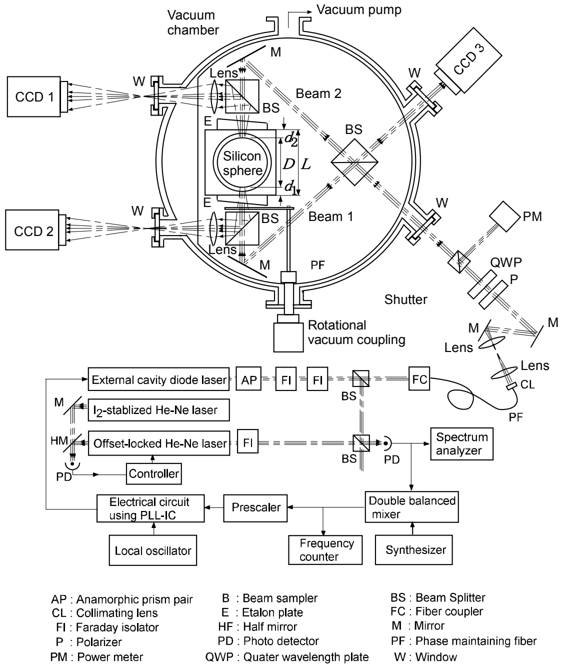

Fig. 2. Block diagram of the interferometer to measure diameters of 1 kg silicon sphere. The lower part of the figure shows a direct optical frequency tuning system.

Each of the changes produces an interference fringe phase shift of $\pi/3$. The interferograms acquired by a computer through the CCD cameras are analyzed to produce a phase profile map. A linear combination of the first six radial Zernike polynominals is fitted to the phase data using a least squares approach and the fractional orders are calculated from this analytic representation at the location of the extremum on each phase map. The required phase shifts are produced by changing the optical frequency of the diode laser using the direct optical frequency tuning system.

Figure 2 show a block diagram of the diameter measurement system. The lower part of this figure shows the optical frequency tuning system. By using this system, the optical frequency of the diode laser can be tuned continuously over a frequency range of 19 GHz and stabilized at a desired frequency. Details of the optical frequency tuning are described elsewhere [9]. The diameter of the sphere, D, is calculated by subtracting the sum of the two gaps ($d_1 + d_2$) from the etalon spacing, L. To determine L, a shutter intercepts beam 1, and the sphere is removed from the light path by a lifting device. Beam 2 passes through a hole in the lifting device, and beams reflected from the two etalon plates produce fringes on CCD 3. These fringes are also analyzed by means of phase-shifting interferometry. The sphere and the etalon are placed in a vacuum chamber with a water jacket. Temperature-regulated water is circulated in the jacket to control the temperature in the chamber. The temperature of the sphere and the etalon is measured by six small 100 Ω platinum resistance thermometers. The thermometers are inserted into copper blocks and attached to the etalon.

3. PROCEDURE FOR DIAMETER MEASUREMENTS

The direction of the sphere is changed by a rotation mechanism installed under the sphere [10,11]. A total of 70 diameters, which are distributed near uniformly all over the sphere, were measured as a function of spherical coordinates. A spherical harmonic function is used to calculate the mean diameter D_m [11]. The volume of the sphere is then obtained as $V=\pi D_m^3/6$. The seventy directions consist of seven sets of ten directions defined by the vertices of a dodecahedron [11]. The etalon spacing was measured before and after each of the ten directions and was used to determine the diameters in the ten directions.

4. RESULTS AND DISCUSSION

4.1 NMIJ Si sphere

In order to evaluate the performance of the interferometer, the volume measurement of a 1 kg silicon sphere S5 was performed. The seventy diameter measurements were repeated four times at 22.500 °C in vacuum. The silicon sphere was fabricated at the Commonwealth Scientific and Industrial Research Organization of Australia (CSIRO) [12]. As the asphericity is of the order of only 80 nm, the volumes can be calculated from the mean of diameter over all directions [13]. The effect of oxide layers on the measured diameter was corrected based on the previous measurements of oxide layers thickness [6]. The volume has been determined with a relative standard deviation of 3.1 × 10^{-8}. The mean diameter for S5, including the oxide layers has been determined with a combined uncertainty of 2.3 nm. The volume at 22.500 °C and 0 Pa is

$V_{S5}=429.624\ 120(31)\ \text{cm}^3$.

The number in the parentheses means the combined standard uncertainty. This expression is also applied in the following sections.

The mass of S5 was determined at the mass standard group of NMIJ. Details of the mass measurement are described elsewhere [14]. The mass in vacuum is

$m_{S5}=1000.612\ 025(15)\ \text{g}$.

The density of S5 is thus determined by its mass and volume at 22.500 °C is 0 Pa to be

$\rho_{S5}=2329.040\ 62(17)\ \text{kg m}^{-3}$.

The relative combined uncertainty in the absolute density measurement is 7.3 × 10^{-8}. Table 1 summarizes the uncertainty sources in the absolute density determination for the silicon sphere. Details of the uncertainties are described elsewhere [6,9,10].

In our previous paper, the relative combined uncertainty of the density of S5 was estimated to be 10.8 × 10^{-8} based on the volume determinations by a scanning-type interferometer [7]. The largest uncertainty source was the random component associated with the volume determinations. Three volume determinations gave the standard deviations of the mean of 9.4 × 10^{-8} [7]. As can be

Table 1. Uncertainty budget in the absolute density determination of a silicon sphere S5 at 22.500 °C and 0 Pa.

Uncertainty source	Standard uncertainty	$10^8\Delta\rho/\rho$
Frequency of laser	10 kHz	0.006
Etalon spacing measurement		
Etalon temperature	3 mK	0.540
Linear thermal expansion coefficient of etalon	3×10^{-9} K^{-1}	0.000
Non-linearity of power meter	0.5 %	0.646
Phase shift in propagation of light beams	0.13 nm	0.417
(d_1+ d_2) measurement		
Sphere temperature	3.2 mK	2.475
Linear thermal expansion coefficient of silicon crystals	1×10^{-8} K^{-1}	0.027
Effect of oxide layers on diameter	2.0 nm	6.409
Non-linearity of power meter for d_1	0.5 %	0.646
Non-linearity of power meter for d_2	0.5 %	0.646
Angular alignment of etalon with optical axis	2×10^{-5} rad	0.039
Phase shift in propagation of light beams	2.4×10^{-4} rad	0.077
Standard deviation of the mean in volume		1.539
Mass in vacuum	15 µg	1.499
Relative combined standard uncertainty		7.317

seen in Table 1, the random component estimated in this work is much smaller than that in the previous work. The major contribution to the uncertainty in the density determination is not the random component but the oxide layers thickness determination. The uncertainty of the thickness was estimated to be 0.5 nm in our previous work [7]. However, taking account of information on recent evaluations of the surface oxide layers, the uncertainty of the thickness measurement is reevaluated to be 1 nm, resulting in a relative density uncertainty of 6.4×10^{-8}. An analysis using x-ray reflectometry (XRR), x-ray photoelectron spectroscopy (XPS) and ellipsometry on the oxide layers are being made at NMIJ for a more accurate measurement of the oxide layers thickness. This may significantly reduce the uncertainty in the density determination. Another major uncertainty source is the sphere temperature measurement. To reduce this uncertainty, a new temperature measurement system is being installed.

As can be seen in table 1, the random component in the volume determination is around 1.5×10^{-8}. Therefore, it will be possible to improve the accuracy of the density of the silicon sphere to a few parts in 10^8 by reducing the uncertainties in the measurements of the oxide layers thickness and the sphere temperature.

4.2 METAS Si sphere and CEM Si sphere

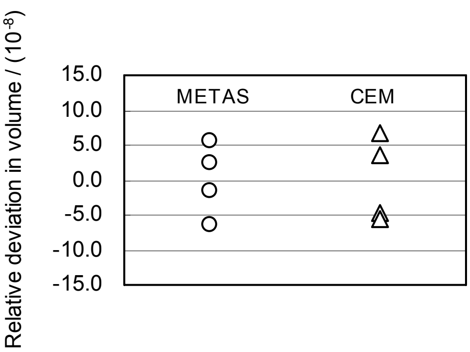

Fig.3 Relavitve deviation of the volume from the mean.

Silicon density standards based on 1 kg silicon spheres have been established by some of NMIs. These density standards have already been disseminated to many NMIs, and are used as a primary density standard. In order to check the long-term stability of the silicon density standards, periodical calibration of the silicon density standards is necessary. As a mutual cooperation between NMIs, NMIJ have performed the absolute volume calibration for 1 kg silicon spheres from Swiss Federal Office of Metrology and Accreditation (METAS, Switzerland) and Centro Español de Metrología (CEM, Spain). The spheres were also fabricated at CSIRO. The seventy diameter measurements were repeated four times for each of the two spheres at 20 °C in vacuum. A spectroscopic ellipsometer (SOPRA, ES4G) was used to measure the thickness of oxide layers on the surfaces of the spheres. The measurements were performed in a wavelength range from 280 nm to 700 nm. Observed dispersion data were then fitted to a theoretical model for a structure of a SiO_2 layer on a Si substrate, in which the optical constants are assumed known and the thickness of the oxide layer and the incident light angle are left adjusted. The measurement was performed at 20 points, which are distributed near uniformly all over the sphere.

The thickness measurements have shown that the mean thickness is 4.58 nm for the METAS sphere and 4.23 nm for the CEM sphere.

Figure 3 shows a relative deviation of the volume from the mean for each sphere. The relative standard deviation of the volume is 5.1×10^{-8} for the METAS sphere and 6.1×10^{-8} for the CEM sphere. The volumes of the two spheres at 20.000 °C and 101 kPa are

$$V_{\mathrm{METAS}} = 429.401\,895(32)\ \mathrm{cm}^3,$$

$$V_{\mathrm{CEM}} = 429.485\,879(33)\ \mathrm{cm}^3.$$

For the conversion of the volumes in vacuum to those at 101 kPa, the isothermal compressibility of silicon crystals [15] is used. The relative combined uncertainty in the absolute volume determination is 7.5×10^{-8} for the METAS sphere and 7.7×10^{-8} for the CEM sphere.

5. CONCLUSION

In this paper, the results on the absolute volume measurements for 1 kg silicon spheres are presented. The relative combined uncertainty of around 7.5 × 10^{-8} has been achieved. The uncertainty analysis has shown that it will be possible to improve the accuracy of the density of the silicon sphere to a few parts in 10^{8} by reducing the uncertainties in the measurements of the oxide layers thickness and the sphere temperature.

The silicon spheres are used as a primary density standard at many NMIs. Accurate density values of the silicon spheres are therefore essential to ensure the confident in the validity of density calibrations at each NMIs. In addition, the present optical interferometer is used for the determination of the Avogadro constant by the XRCD method [8]. The measurement accuracy of the Avogadro constant which can be achieved at present is approximately 10^{-7}. If this can be improved by one order, it is possible to redefine the kilogram according to a defined number of atoms. The present interferometer thus plays an important role not only in basic metrology but also in the front line of research on standards.

REFERENCES

[1] K. Fujii, A. Waseda, and N. Kuramoto, “Development of a Silicon Density Standard and Precision Density Measurements of Solid Materials by Hydrostatic Weighing,” Meas. Sci. Technol., Vol. 12, pp. 2031–2038, 2001.

[2] M. J. Kenny, A. J. Leistner, C. J. Walsh, K. Fen, W. J. Giardini, L. S. Wielunski, R. P. Netterfield, and B. R. Ward, ”Precision Determination of the Density of a Single Crystal Silicon Sphere and Evaluation of the Avogadro Constant,” IEEE Trans. Instrum. Meas., Vol. 50, pp. 587–592, 2001.

[3] R. A. Nicolaus and G. Bönsch, “Absolute volume determination of a silicon sphere with the spherical interferometer of PTB, Metrologia, Vol. 42, pp. 24–31, 2005.

[4] A. Sacconi, A. Peuto, M. Mosca, R. Panicera, W. Pasin, and S. Pettorruso, “The IMGC Volume-Density Standards for the Avogadro Constant,” IEEE Trans. Instrum. Meas., Vol. 44, pp. 533–537, 1995.

[5] Le Système International d’Unités (SI), 7 th ed., Sèvres, Bureau International des Poids et Measures, 1998.

[6] K. Fujii, M. Tanaka, Y. Nezu, A. Sakuma, and A. Leistner, “Absorlute Measurement of the Density of Silicon Crystals in Vacuo for a Determination of the Avogadro Constant,” IEEE Trans. Instrum. Meas., Vol. 44, pp. 542–545, 1995.

[7] K. Fujii, A. Waseda, N. Kuramoto, S. Mizushima, M. Tanaka, S. Valkiers, P. Taylor, R. Kessel, P. De Biévre, “Evaluation of the Molar Volumes of Silicon Crystals for a Determination of the Avogadro Constant,” IEEE Trans. Instrum. Meas., Vol. 52, pp. 646-651, 2003.

[8] K. Fujii, A. Waseda, N. Kuramoto, S. Mizushima, P. Becker, H. Bettin, A. Nicolaus, U. Kuetgens, S. Valkiers, P. Taylor, P. De Biévre, G. Mana, E. Massa, R. Matyi, E. G. Kessler, Jr., and M. Hanke, “Present State of the Avogadro Constant Determiantion From Silicon Crystals With Natural Isotopic Compositions,” IEEE Trans. Instrum. Meas., Vol. 54, pp. 854-859, 2005.

[9] N. Kuramoto, and K. Fujii, “Interferometric Determination of a Silicon Sphere Using a Direct Optical Frequency Tuning System,” IEEE Trans. Instrum. Meas., Vol. 52, pp. 631–635, 2003.

[10] N. Kuramoto and K. Fujii, “Volume Determination of a Silicon Sphere Using an Improved Interferometer with Optical Frequency Tuning,” IEEE Trans. Instrum. Meas., Vol. 54, pp. 868–871, 2005.

[11] A. Sakuma, K. Fujii, and M. Tanaka, ”Experimental determination of the volume of a crystalline silicon sphere using spherical harmonics,” Meas. Sci. Technol., Vol. 5, pp. 1233–1238, 1994.

[12] A. J. Leistner and W. J. Giardini, “Fabrication and Sphericity Measurements of Single-crystal Silicon Spheres,” Metrologia, Vol. 31, pp. 231–243, 1994.

[13] D. P. Johnson, “Geometrical Considerations in the Measurement of the Volume of an Approximate Sphere,” J. Res. Natl. Bur. Stand. Sect. A, Vol. 78, pp. 41–48, 1974.

[14] S. Mizushima, M. Ueki, and K. Fujii, “Mass Measurement of 1 kg silicon spheres to establish a density standared,” Metrologia, Vol., 41, pp. S68–S74, 2004.

[15] H. J. McSkimin and P. Andreatch, Jr, “Elastic Moduli of Silicon vs Hydrostatic Pressure at 25.0 °C and −195.8 °C,” J. App. Phys., Vol. 35, No.7, pp. 2161-2165, 1964.