Determination of Mean Thickness of an Oxide Layer on a Silicon Sphere by Spectroscopic Ellipsometry *

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One of the biggest obstacles to reduce the uncertainty of the Avogadro constant N_A is such that there will be an oxide layers on the surface of a silicon sphere. The thickness of this layer is measured by a modified spectroscopic ellipsometer, which can eliminate the influence of the curved surface, and the results are calibrated by x-ray reflectivity. Fifty positions distributed nearly uniformly on the surface of the silicon sphere are measured twice. The results show that the mean thickness of the overall oxide layer is 3.75 nm with the standard uncertainty of 0.21 nm, which means that the relative uncertainty component of N_A owing to this layer can be reduced to 1.2×10^{-8}.

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The accurate measurement of the Avogadro constant N_A is a promising route to redefine the kilogram (unit of mass) if its combined uncertainty can be reduced to 2×10^{-8} or less from current 5×10^{-8}.[1] N_A can be described by the formula $N_A = (M_m/\rho)/(V_0/n)$, where M_m is the mole mass, ρ is the macroscopic density of crystal, V_0 is the volume of the unit cell, and n is the number of atoms in the unit cell. The x-ray crystal density (XRCD) is considered the most precise method to determine N_A.[2] In this method, a perfect single crystal silicon sphere with the mass of approximate 1 kg and diameter of nearly 94 mm is applied to determine the crystal density ρ. Among the above four parameters, the standard uncertainty of density ρ is one of the biggest obstacles.[3,4] The reason is that the oxide layer, grown on the sphere's surface during the process of fabrication, has great influence on the measurement of the sphere's diameters.[5] According to Ref. [5], the oxide layer with 1 nm thickness would result in an error of nearly 1.9 nm in diameter of the sphere when applying the laser interferometer with the wavelength of 633 nm. When considering the definition of N_A, this 1 nm oxide layer would introduce the uncertainty of nearly 6×10^{-8} to N_A, three times larger than the expected result.

Much attention has been paid to this layer,[4,6,7] and the most recent result is given by Kuramoto *et al.*[8] In Kuramoto's paper, this layer was measured at 20 different positions by spectroscopic ellipsometer (SE) with a light beam larger than 2 mm, and the techniques of x-ray reflectivity (XRR) and x-ray photoelectron spectrometer (XPS) were applied to test the results of SE and the chemical composition of the layer. However, they did not eliminate the effect of spherical curvature on the ellipsometer's results, which would introduce error to the SE results. Moreover, they tested the accuracy of the SE just by comparing the measurement consistence with XRR on two thermal oxidization disks, which was an improper calibration method because they can not deduce the calibrated results with the specific measured thicknesses of the oxide layer. In addition, twenty positions may not be sufficient because the thicknesses of this layer are not uniform but varied with the orientation of the single crystal silicon sphere.

In this Letter, the thickness of the oxide layer and the roughness of the silicon sphere are determined by the SE and 3D-surface profiler, and the accuracy of SE was calibrated by XRR. Fifty points which were distributed approximately uniformly on the surface of the sphere were measured twice by SE.

SE is widely used in analyzing the thickness and the refractive index of the thin films.[9–11] The measurement principle of SE is described by $\tan\psi \exp(i\Delta) = \rho = R_p/R_s$, where (ψ, Δ) are measured by ellipsometry, ρ is the ratio of the reflection coefficients of p-polarization R_p and s-polarization R_s. Different from the usual application of SE on plane sample, e.g., silicon wafer, the curvature surface of the silicon sphere would make the reflected light divergent for the incident parallel beam, as shown in Fig. 1. An optical software ZEMAX is applied to demonstrate this effect, and the result is presented in Fig. 2. Left part of Fig. 2 demonstrates the beam spot with incident angle of 70° and diameter of 1 mm, and the

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right part is the reflected spot received by the detector. Because of the reflection on the spherical surface, the 1 mm beam spot becomes an ellipse with long and short axis of 48.2 mm and 6.7 mm, respectively. It is clear that the spherical surface makes the angles of the incident parallel beam changing with positions after reflection. Except for the top point of the sphere, the reflected angles in all of the illuminated positions are deviated from the initial incident angle of the parallel beam. If the whole reflected beam is analyzed by the detector, the depolarization caused by the varied angles will introduce potential errors to the SE results.

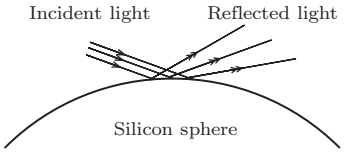


Fig. 1. Light reflection on the surface of the silicon sphere.

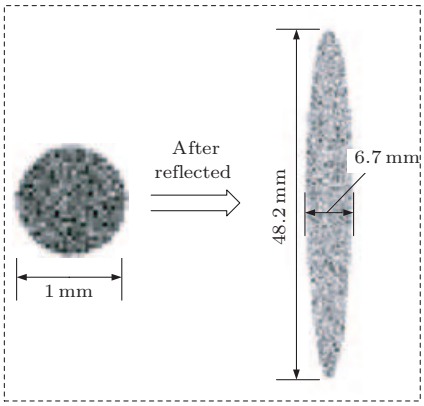


Fig. 2. Simulation of the reflected light on the surface of the silicon sphere by ZEMAX.

A modified setup of SE is applied to eliminate almost completely the depolarization effect by selecting the central area around the top point of the sphere to analyze. As shown in Fig. 3, settling the detector D far from the top point of the sphere, e.g., 376.1 mm, and putting a slit S3 with diameter of 1 mm in front of it, therefore, the incident lights which can be received by the detector are in the range of $70° \pm 0.04°$. This difference can hardly be resolved by the SE.

The silicon sphere is made of single crystal silicon with a purity of better than 99.9999%, and fabricated in China. The fabrication is similar to the process of optical fabrication. Different from glass, however the single crystal silicon is anisotropic, and the variation of Young's modulus with crystal orientation will lead to the deviation from sphericity of the sphere in different directions. Likewise, the thicknesses of the oxide layer will change with the positions on the sphere.[12] The final diameter of the sphere is about 93.6 mm. The roughness is measured by the 3D-surface profiler, and the results on two different orientations are shown in Fig. 4. The roughness of the surface on most of positions are uniform, and the final roughness of the whole surface is determined to be $R_a = 4.60$ nm with standard uncertainty of 0.10 nm.

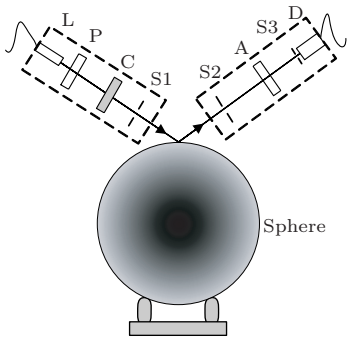


Fig. 3. Measuring oxide layer of silicon sphere by SE. The left and right dashed rectangles represent the incident and receiving arms of SE, respectively. In the incident arm, the parallel beam from the light source L passes through polarizer P, compensator C and slit S1 in turn, and illuminates the top point of the silicon sphere S. Then the reflected light is received by the receiving arm, which consists of silt S2 and S3, analyzer A and detector D.

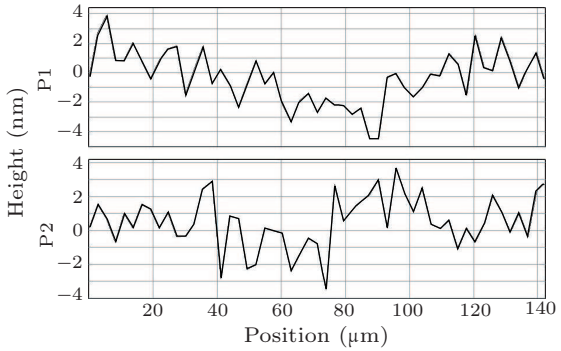


Fig. 4. Typical 2D line profile of the polished silicon sphere in two orientations P1 and P2. X-axis represents the position on the spherical surface, Y-axis represents the vertical deviation of the surface.

The SE utilized is a product of Sentech Company, and light source with spectral range between 190 nm and 400 nm (with step of 0.8 nm) is applied because most features of single crystal silicon are in this range; the size of incident beam is set as 1 mm, and the automatic collimating telescope is applied to make sure the incidence light illuminate on the top point of the silicon sphere.

Different from the thermal oxidation having nearly 100% SiO_2, The native oxide layer, generated in the process of fabrication, usually contains suboxides.[6] The mixture of monoxide silicon and dioxide silicon $(SiO)_a(SiO_2)_{1-a}$ $(0 < a < 1)$ is applied to represent this layer. The theoretical model of the oxide layer is shown in Fig. 5. The optical constants of the crystalline silicon (c-Si), SiO and SiO_2 come from the Aspnes and Piller's published data,[13–15] and the effective medium approximation (EMA) theory is em-

ployed to model the roughness and the native oxide.[9] Figure 6 shows the result of SE on one point. The MSE on all the points have an average of 0.51 with the standard deviation of 0.13, which indicates that the theoretical model is valid. According to the EMA theory, the roughness is considered as a homogeneous film with void in the host material (native oxide film). The volume fraction of the void is determined to be $f_{\text{void}} = 0.563$. The refractive index of the roughness equals to 1.192 at 633 nm. The native oxide layer consists of 8% SiO and 92% SiO_2.

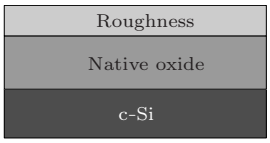


Fig. 5. Optical model applied in SE data analysis.

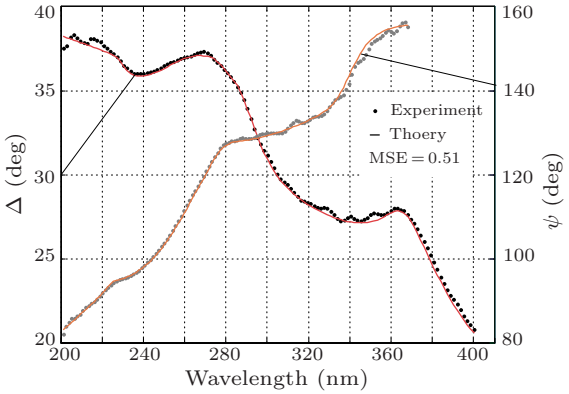


Fig. 6. Measurement result of the SE at single point. X-axis represents the wavelength of the light source, and the Y-axis represents the measured elliptical angles PSI and DELTA.

Table 1. Summary of the SE measurement results.

Sampling points	Mean thickness (nm)
1^{st} 50 points	3.79
2^{nd} 50 points	3.81
100 points	3.80

To obtain the mean thickness of the layer on the whole surface, fifty points distributed nearly uniformly on the surface of the sphere are measured by the SE, and the measurement repeats randomly once again. All the rotations of the sphere are achieved by the homemade rotation mechanism automatically. The measurement results are shown in Fig. 7 and listed in Table 1. According to the results, fifty-points can almost represent the true distribution of the thickness of the oxide layer. Repeated measurement shows the results are highly consistent. Thus the final mean thickness of the oxide layer on the silicon sphere can approximately be estimated by averaging one hundred points, namely, $\bar{t} = 3.80$ nm, and the difference 0.02 nm of the two measurements can be considered as the repeatability of the mean thickness.

In order to evaluate the accuracy of the SE, the XRR method, which can measure the true thickness (independent of the optical index) of the film accurately, is applied to calibrate it. Five thermal oxidization SiO_2 films with different thicknesses on single crystal silicon wafers are prepared, and the results measured by XRR and SE are fitted by a straight line. Calibration result is expressed by $d_{SE} = (1.013 \pm 0.013) d_{\text{XRR}}$. More details can be found in Ref. [16]. According to the calibration line, the standard deviation of the calibrated SE does not exceed 0.09 nm for the film thinner than 7 nm (the upper limit thickness of overall points on the sphere), with the calibrated mean thickness of 3.75 nm. The repeatability of SE is estimated by measuring the same position for ten times, and the standard deviation is 0.05 nm, as shown in Fig. 8. Therefore, the experiment yields the combined uncertainty of the mean thickness of 0.11 nm.

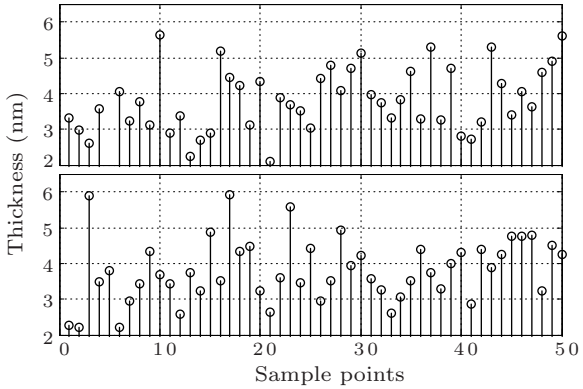


Fig. 7. Thickness of the oxide layer by twice measurements.

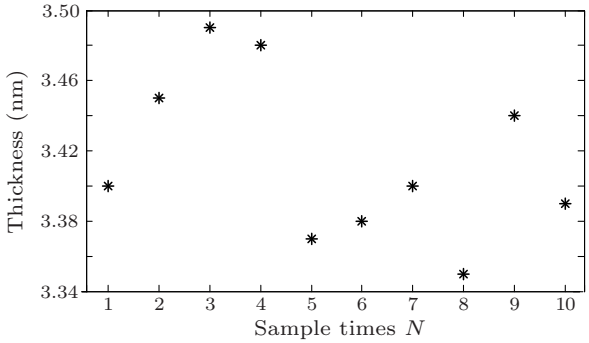


Fig. 8. Measurement repeatability of the SE by ten times.

In summary, in order to compensate for the error of the mean diameter caused by the oxide layer, the mean thickness of the overall oxide layer should be determined accurately. A modified SE is applied to determine the thickness of the oxide layer at fifty positions distributed uniformly on the silicon sphere, and the mean thickness of the oxide layer is determined to be $\bar{t} = 3.75$ nm with the standard uncertainty of 0.11 nm.

Considering the uncertainty of roughness, the uncertainty of the oxide layer will not exceed 0.21 nm, which yields the relative uncertainty component of N_A of 1.2×10^{-8} after correcting the error introduced to the sphere's diameter. This result is in the acceptable level for the Avogadro project when compared with the target combined uncertainty 2×10^{-8} of N_A.

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