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Full Length Article

Application of ellipsometry for the accurate oxide layer measurement on silicon spheres

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ABSTRACT

As one of the reference measurement methods for future realization of the unit of mass (kilogram) and Avogadro constant N_A, the silicon (Si) sphere method employs the ellipsometry for the measurement of the thickness of the ultrathin (<10 nm) silicon oxide layer (OL) with high accuracy. Depending on the reference standard used, the application of ellipsometer is generally divided into the internal and external calibrations, respectively. For the former, the Si sphere itself is used as the reference standard to directly compare the ellipsometric and another independent high-accuracy thickness measurement method, thus achieving an uncertainty of $u(d_{OL}) \approx 0.1$ nm. For the latter, the uncertainty is enlarged because the transfer standards of wafer samples are essentially not the same as the Si sphere. In spite of the different level of uncertainty, the external calibration method provides more practical approach for dissemination and maintenance of the new mass unit. Both methods are studied in detail for practical guidance.

1. Introduction

Currently a new fundamental setup of the international system of units (System International, SI) is being prepared by metrologists worldwide. With this new SI, awaited to be installed in 2018, a new definition of the unit of mass (kilogram) will be implemented. The kilogram is the last base unit defined by an artifact stored in a vault at the Bureau International des Poids et Mesures (BIPM) in Sèveres, France. The new definition of the kilogram will be based on the Planck constant h [1].

For this purpose, the determination of h with unprecedented high accuracy is carried out by different experiments, i.e., the Watt-balance experiment [2] and the X-ray crystal density (XRCD) experiment [3]. The XRCD determines the Avogadro constant N_A, which is linked via the molar Planck constant with h. The molar Planck constant is known with a relative uncertainty of 4.5×10^{-10}. Hence, from this experiment h can be calculated without a significant loss of accuracy, if the relative uncertainty for N_A is in the order of 10^{-8}. Therefore both experiments will make a contribution to the new kilogram.

The general principle of the XRCD experiment can be formulated as:

$$\frac{m}{V} = \frac{nM/N_A}{a^3}, \quad (1)$$

where m is the mass and V the volume of the sphere, i.e. the macro density of the sphere. The second part of the equation is the microscopic density of the Si crystal with the lattice constant a, the molar Mass M and the number of Si atoms in the unit cell n. For the determination of N_A highly enriched ^{28}Si spheres are used [3].

Unfortunately the Si spheres are covered by a surface layer (SL), consisting of an oxide layer (OL) accompanied by an additional water layer (chemisorbed and physisorbed water, CWL/PWL) and carbonaceous contamination layer (CL). The mass m_{SL} and the thickness d_{SL} must be determined as correction factors for the mass and volume determination of the sphere, since the mass and volume of the Si core must be measured.

Since it is required to determine the average thickness (and mass) of the surface layer, several thousand data points, uniformly distributed over the sphere surface, are required, on one aspect, to keep the statistical uncertainty of the average thickness within the required limit.

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2. Surface characterization

2.1. General considerations

The demand to characterize the whole sphere surface defines some requirements for the appropriate measurement technology, namely: (1) non-destructiveness; (2) fast data acquisition; (3) sensitive for ultrathin oxide layer ($d \approx 1$ nm); (4) accurate ($u(d) \approx 0.1$ nm); (5) precise and accuracy achievable with calibration. The requirements (1) to (3) are readily fulfilled by spectroscopic ellipsometry (SE), but on the other hand SE is not accurate enough without calibration [4]. For the calibration, generally two different options are present: the so called internal calibration using the sphere itself as reference, or the external calibration using external reference artifacts.

2.2. Challenges for implementing ellipsometry

To measure the surface of the Si sphere by ellipsometry, one is faced with several challenges. Firstly, as an inverse method, the ellipsometry requires the knowledge of the optical constants to get the unique thickness values, and vice versa. Otherwise, the regression analysis often would not work well in the case of ultrathin films. Unfortunately the optical constants for the ultrathin SiO_2 film are different from the published values [5,6]. This is an extensively studied topic. We tried a different method by firstly determining the thickness independently and then inversely deducing the refractive index of the ultrathin SiO_2 films. To keep the reader on the main thread of the present work, the detailed discussions are referred to Appendix A.

Secondly, the measurement at curved surfaces requires a careful alignment of the sphere. We checked the thickness deviations as the apex of the sphere-crown Si sample moves away relative to the measurement plane. While an in-plane movement (0.4 mm) gave rise to negligible deviations as compared to the short-term repeatability of the ellipsometer (0.01 nm), the out-of-plane movement (0.5 mm) results in an observed deviation in thickness of at least 0.04 nm. It is noted that this result could be different from one instrument to another. However, for internal calibration, the error in thickness due to the misalignment could be corrected so long as the relative position of the sphere is kept stable enough during the measurement. Another issue associated with the curved surface is the light beam divergence and potential depolarization. Luckily the problem is not severe as one might expect. For a discussion and experiment with Mueller ellipsometry, readers are referred to Appendix B.

Last but not least, for external calibration the reference standards must be as close to the properties of the target system (in this case the Si spheres) as possible. Beside the already mentioned optical constants, other properties like the roughness or sub-surface damages must be taken into account. With internal calibration this condition is inherently fulfilled. Furthermore, with internal calibration, the measurement deviations stemming from the alignment or the simulation model can be tolerable, if only the accuracy is affected, without changing the precision of the ellipsometric measurements. Table 1 gives an overview of the different influences to the accuracy and precision.

3. Instrumentation

The spectroscopic ellipsometer of PTB is a GES-5E manufactured by Semilab™, and that of NIM is a SE800 by Sentech™ (Fig. 1). The instruments have been modified to meet the specific requirements of sphere measurements. A special sphere sample holder with a friction wheel support is installed for the mapping task (Fig. 2). With this sample holder the whole surface is accessible to measurement with two orthogonal rotational axes θ and φ. Furthermore the θ-axis is perpendicular to the plane of incidence of the ellipsometer, therefore requiring that the plane of incidence be the horizontal plane. This mechanical structure also has the benefit of reducing the contact area between the supporting wheel and the sphere surface, which further reducing the opportunity of contamination.

Table 1
Overview of parameter influencing the uncertainty of measurement regarding to accuracy and precision.

Parameters	Influences to	
	accuracy	precision
optical constants	yes	minor
alignment of sphere	yes	no
stability of alignment during measurement	yes	yes
mechanical properties of surface	yes	no
simulation model	yes	minor
linearity of model	yes	yes

Similar to the grid on a terrestrial globe, a great meridian circle of data points is formed by θ-scan with inclination φ in the step $\Delta\varphi = 10°$. The complete mapping grid of the sphere surface is divided into two data sets (A and B) of great circles. Mapping A starts with $\varphi = 0°$ to and ends at 170°, while for mapping B, φ scans from 5° to 175°.

A complete mapping of the sphere can be finished within 24 h. During the mapping, the sphere is aligned with the φ-axis directing through one of the three calibration marks, thus ensuring that each θ-scan includes the same calibration point for every φ inclination.

With the statistical data refined from the two mappings A and B, such as thickness range, standard deviation and weighted thickness, the integrity or consistency of both data sets can be checked. Discrepancies are indication for false data acquisition within the mappings A or B. This is used to improve the reliability of the combined data set, which are finally merged to calculate the average thickness ($d_{OL,ave}$).

4. Internal calibration

With the internal calibration the ellipsometer is used as a comparator, since the data from the ellipsometric measurements are compared to the data from a known reference on the sphere with known thickness measured by an independent calibration method with the required uncertainty of $u(d) \leq 0.1$ nm. In the following the ellipsometric result is calibrated by a calibration constant derived from the three thickness values at the calibration points.

$$d = d_{SE} + c \tag{2}$$

Typically three calibration points are established on a single sphere, identified by different markings ("+" and "T" at (100) lattice plane and "Δ" at the (111) lattice plane). The calibration points are on the opposite side of the markings, i.e. at 180° on a great circle with the marking at 0°. At PTB, a combination of X-ray reflectometry (XRR) and X-ray fluorescence analysis (XRF) has been successfully used as the calibration method for the calibration of the SE [7].

For the uncertainty of the average film thickness beside the statistical component, three uncertainty components have to be taken into account: (1) the uncertainty of the thickness value at the calibration point; (2) the short-term stability of the ellipsometer, and (3) the uncertainty of the calibration constant c. The first uncertainty is given by the accuracy of the calibration method. The second component is estimated by a reproducibility measurement to be $u(d_{OL}) = 20$ pm. The last component is given by the local topography of the oxide layer, i.e., the variation of d_{OL}, at the calibration point. To evaluate this component, firstly the uncertainty of position of

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