Development of a combined XRF XPS surface analysis system

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Abstract: At 26th meeting of CGPM in Nov. 2018, the definition of the unit of mass, the kilogram, is redefined by a fixed value of Planck constant h = 6.626 070 15*10^{-34} J s to replace the International Prototype of the Kilogram (IPK). One of the primary methods to realize the definition is the XRCD method (X-ray crystal density method) with a ^{28}Si-enriched sphere whose mass can be expressed in terms of the number of Si atoms inside and take the mass of the surface layer into account.

The quantitative surface analysis of ^{28}Si-enriched spheres is characterized via a combined x-ray fluorescence (XRF) and x-ray photoelectron spectroscopy (XPS) analysis system. The surface layer is mainly composed of oxide layer, carbonaceous contamination and water. To identify the chemical elements and determine the mass present in a surface, the newly combined instrument was implemented to measure the XRF for the mass deposition of oxygen (ng/cm^2) with the silicon-drift-detector tested and calibrated by PTB and the XPS for the ratio between the elements (O, Si, C). These two complementary methods of x-ray metrology allow an accurate determination of the mass of the surface layer which is applied to the realization of the kilogram by XRCD method.

The national measurement laboratory (NML) in Taiwan has established the combined XRF XPS surface analysis system in 2019. The construction work including the assembly of parts of the load lock chamber and UHV analysis chamber, software, hardware integration and light path adjustment was preliminarily completed. To give the mass of the ^{28}Si-enriched sphere, the mass of the surface layer measured by the combined XRF XPS surface analysis system should be monitored for its stability and combined with the mass from the core of the sphere. However, since the measurement of the surface layer is carried out under vacuum (10^{-9} mbar), the sorption correction for evaluating the mass difference of the mass standards transferred between in air and in vacuum have to be considered for mass dissemination.

Keywords: XRCD, Si-sphere, XPS, XRF

1. INTRODUCTION

At 26th meeting of CGPM in 2018[1], the definition of the unit of mass, the kilogram, is redefined by a fixed value of Planck constant h = 6.626 070 15*10^{-34} J s to replace the International Prototype of the Kilogram (IPK) and the new definitions came into force on 20 May 2019 [2,3]. There are two primary methods to realize the definition of the kilogram: comparing electrical power to mechanical power [4,5] and X-ray-crystal-density method [6-8]. With the transmission of the information and technology from Physikalisch-Technische Bundesanstalt (PTB), the national measurement laboratory (NML) adopted the X-ray-crystal-density method and established the combined XRF XPS surface analysis system for evaluating the surface mass of the Si-sphere. In this paper, we report the current progress and the intended work of the construction of the XRF XPS surface analysis system.

2. THE SURFACE LAYER MODEL OF THE ^{28}SI-ENRICHED SPHERE

On the basis of the x-ray-crystal-density method, the core mass m_{core} of the Si-sphere is determined by counting the number of atoms inside a ^{28}Si-enriched sphere and multiply with its mean molar mass of the Si. However, the oxide layer is formed on the sphere surface. The mass of the Si-sphere m_{sphere} should take the mass correction of the surface layer into account:

$$m_{sphere} = m_{core} + m_{SL}, \tag{1}$$

The surface layer (SL) model (Fig. 1) used for the Si-sphere is composed of an oxide layer with SiO_2 and suboxides (Si_2O, SiO, Si_2O_3) at the interface on top of the bulk silicon crystal and carbonaceous contaminations (CO_x,C) as well as water layer. To identify the chemical elements and determine the mass present in a surface, an accurate evaluation of surface layers by x-ray photoelectron spectroscopy (XPS), and x-ray fluorescence (XRF) spectrometry is being conducted [9].

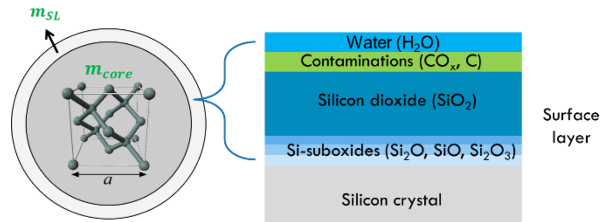

Fig.1 The model of the surface layer of the Si-sphere

3. SURFACE CHARACTERIZATION

3.1 X-ray fluorescence (XRF)

X-ray fluorescence (XRF) is a typical method for elemental and chemical analysis. The characteristic x-ray is emitted from a material that has been excited by being bombarded with high-energy x-ray

or gamma-ray (Fig. 2).

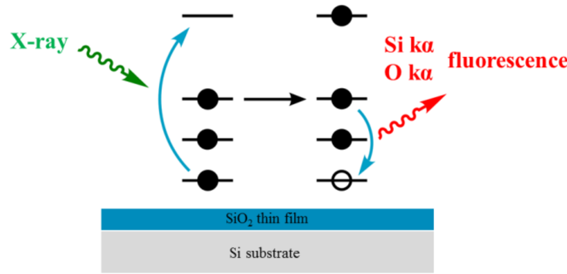

Fig.2 The schematic diagram of x-ray fluorescence from a SiO_2 thin film with thickness of several nanometers.

For Si-spheres, XRF is utilized to measure the surface density, i.e. the deposition mass (ng/cm^2), of the oxygen present in the surface layer. Since the in-house x-ray source is not stable enough for element quantification, the synchrotron radiation-based reference-free X-ray fluorescence analysis [10-12] is employed for the quantification approaches of the deposition mass of oxygen. With this technique, the intensities of O kα and Si kα are measured at BESSY II from 5 SiO_2 reference samples with the nominal thickness ranging from 2 nm to 10 nm. According to Sherman's equation, the correlation of the mass deposition in relation to its fluorescence radiation of O kα/Si kα intensity is given:

$$md_O = -\frac{G}{\mu_{tot}} ln(1 - C_0 R_{OSi} \mu_{tot}) \quad (2)$$

where md_O is the mass deposition of oxygen, C_0 is the calibration factor, μ_{tot} is the total mass attenuation coefficient, G is the geometry factor and R_{osi} is the ratio of the measured intensity of the fluorescence radiation of O kα/Si kα. Most of the Si kα signal comes from the Si substrate. The ratio of O kα/Si kα reflects the amount of change in oxygen. The mass deposition of oxygen of the Si-sphere surface layer is obtained by interpolation using the correlation curve of the mass deposition of oxygen and O/Si ratio referred to the reference samples.

3.2 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive measurement technique. The photoelectrons escape from the sample as the x-ray energy irradiating on the sample is larger than the binding energy of the elements. The kinetic energy of the photoelectrons is analyzed by an electron spectrometer to identify the chemical elements and their binding states (chemical shift) (Fig.2).

Without reference samples used for XPS measurement, only ratios between Si *2p*, O *1s* and C *1s* are quantified according to the amount of the photoelectrons detected. In the surface layers, the relative atomic fraction C_A between the elements is

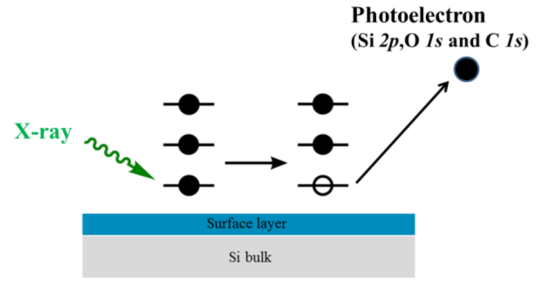

Fig.3 The schematic diagram shows the photoelectrons escaping from the surface layer of Si-sphere.

obtained by the normalized XPS signal I_{jA}' :

$$I'_{jA} = \frac{I_{jA}}{\sigma_{jA} \cdot \lambda(KE) \cdot T(KE)} \quad (3)$$

where $T(KE)$ is the transmission function, σ_{jA} is photoelectric cross section of photoemission j of element A [13] and $\lambda(KE)$ is the inelastic mean free path of the photoelectrons [14]. And the atomic fraction can be expressed as following:

$$C_A = \frac{I'_{jA}}{\sum I'_{jA}} \quad (4)$$

With the ratios between the elements measured by XPS, the absolute mass depositions of Si and C can be calculated by the mass deposition of oxygen in the surface layer based on XRF. The detailed XPS scans of Si *2p* and C *1s* give the ratios corresponding to different binding states. For example, there are several peaks in the XPS scan in Si *2p* including silicon in the bulk, in the silicon dioxide (SiO_2), and in the various suboxides (Si_2O, SiO and Si_2O_3) in the interface. The distribution of the oxygen present in the silicon oxide layer and carbonaceous layer can be evaluated by stoichiometric approach.

Since the hydrogen can't be measured by XPS, The mass deposition of hydrogen is estimated and addressed by the possible molecules in carbonaceous layer. For the water layer, the estimation of mass deposition of hydrogen relies on the remaining oxygen and the silicon hydroxyl group in silicon oxide layer [15].

4. CONSTRUNTION OF XRF XPS SURFACE ANALYSIS SYSTEM

The national measurement laboratory (NML) is establishing the combined XRF XPS surface analysis system in 2019. This system allows the complementary measurement of XRF and XPS emitted by the surface of Si-spheres. The construction work including the assembly of parts of the load lock chamber and ultra-high-vacuum (UHV) analysis chamber, software, hardware integration are in progress. The design of the combined XRF XPS system is showed in Fig. 4. The system is mainly composed of 2 chambers: The loadlock chamber and the UHV analysis chamber. The Si-sphere is placed in the loadlock chamber and transferred into the UHV-analysis chamber to carry out the XPS and XRF measurement. The radiation of the

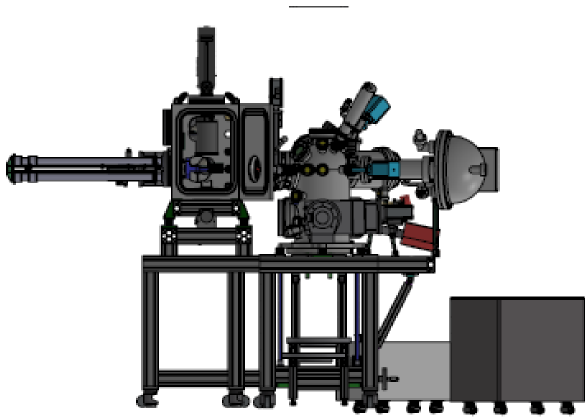

Fig. 4 The design of the combined XRF XPS surface analysis system.

characteristic Al Kα fluorescence line is 1486.6 eV with quartz crystal in Rowland geometry to monochromatize. The geometry between the excitation radiation and the photoelectron detection channel (electron spectrometer) is fixed at the magic angle of 54.7° with the pass energy of 80 eV for spectrum survey and 40 eV for detailed scan. The fluorescence detection channel (a windowless 60 mm² silicon drift detector) is set up with respect to the incident radiation at angles of 45° out of plane and 15° in plane. The key component of the instrument is the UHV 5-axis manipulator to investigate the full Si sphere surface in different geometries inside the UHV-analysis chamber (Fig. 5). For the 5-axis manipulator, 2 of the axes are linear motors moving along the vertical and horizontal directions respectively to adjust the position of the Si-sphere to the center of the chamber. The other three axes are composed of rotating motors. The motor at the lowest is to rotate around the center of the UHV analysis chamber to change the angle of incidence on the Si-sphere. The upper two motors rotate around the horizontal and vertical axis respectively with center of the Si-sphere to measure the element distribution on the Si-sphere.

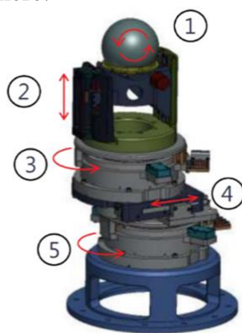

Fig. 5 The schematic view of the UHV 5-axis manipulator. The axes ① and ③ are rotated around the center of the Si-sphere the axis ⑤ is rotated around the center of the chamber and the axes ② and ④ move linearly to adjust the position of the Si-sphere.

Now the combined XRF XPS surface analysis system is being assembled. The degree of vacuum of loadlock chamber is of 10^{-7} mbar and UHV analysis is of 10^{-9} mbar. For the preparation of XRF measurement, in addition to the silicon drift detector (SDD) has been calibrated the response function and detector efficiency from 100 eV to 1850 eV [16], the mass deposition of oxygen of the five SiO_2 reference samples with thickness of 2 nm, 4 nm, 6 nm, 8 nm and 10 nm were also measured by PTB.

5. FUTURE WORK

To measure and characterize the surface layer mass of the Si-sphere, the future work can be divided into two directions to be discussed. In the first phase, the pre-processing work before starting the XRF and XPS measurement of the Si-sphere is expected to be completed: The hardware and software control system will be integrated. The light path is adjusted to pass through the center of the chamber and the sample is aligned for the angle of incidence of XRF and XPS measurement respectively. For XRF measurement, the calibration curve for the mass deposition of oxygen from the series of SiO_2 reference samples by reference-free X-ray fluorescence analysis with the O/Si intensity ratio measured by the combined XRF XPS surface analysis system should be fitted according to eqn.(2). For XPS measurement, as one of the factors for intensity normalization, the transmission function $T(KE)$ of the electron spectrometer is required to be determined with the QPA method by measuring Ag, Au, and Ge reference samples with the pass energy of 40 eV and 80 eV [17]. In the second phase, the expected goal is to give the surface layer mass and uncertainty of the Si-sphere. First of all, the XPS or XRF measurement should be repeated the scan over the Si-sphere several times to check for the angular setting liability of the UHV 5-axis manipulator. The measured O/Si fluorescence intensity of the Si-sphere is interpolated by the fitted calibration curve to obtain the mass deposition of oxygen present in the surface layer. Then the XPS measurement is carried out around the full surface of the Si-sphere to calculate the ratio of photoelectrons between Si, C and O. The uncertainty of the mass of the surface layer will be evaluated from the source for XRF measurement including the calibrated mass deposition of the SiO_2 reference samples, the fitted O/Si ratios and the reproducibility.

To give the mass of the ^{28}Si-enriched sphere, the mass of the surface layer measured by the combined XRF XPS surface analysis system should be monitored for its stability and combined with the mass from the core of the sphere. However, since the measurement of the surface layer is carried out under vacuum (10-^{9} mbar), the sorption correction for evaluating the mass difference of the mass standards transferred between in air and in vacuum have to be considered for mass dissemination.

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