DETERMINATION OF ADSORTION LAYERS ON SILICON SORPTION ARTIFACTS USING MASS COMPARISON

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Abstract: The adsorption layers on the surface of silicon artifact have been determined experimentally as a function of relative air humidity in the range of $0.07 < h < 0.73$ using gravimetric method. For the purpose of this work 1 kg silicon sorption artifacts were fabricated, which have same surface finish, material properties but with very different surface area of 507.8 cm^2. In this experiment ultra precision mass comparator and special humidity control unit were used. The adsorption isotherm of water vapor on the silicon surface with $R_z < 26.6$ nm measured and sorption behavior of silicon surface is being type II by BET classification, BET parameters μ_m=0.017 μg/cm^2, c_B=9.3 were found. The coefficient of water vapor adsorption in moist air was δμ/δh=65.3 ng cm^{-2} $\%^{-1}$ in the limited humidity range of $0.3 < h < 0.6$.

Keywords: silicon sorption artifacts, mass comparison, adsorption layer

1. INTRODUCTION

Nowadays international efforts have been underway to redefine the unit of mass by relating it to either Planck constant using watt-balance experiment or to Avogadro constant N_a using a silicon sphere (x-ray crystal diffraction) method to realize the definition with sufficiently small uncertainty so as to allow current definition of the kilogram could be replaced [1]. Both of these approaches require realization of the kilogram in vacuum condition. Currently the kilogram artifact is stored and used in air therefore due to the air-vacuum transfer accurate knowledge of sorption induced mass change has to be considered, which is determined usually by means of sorption artifacts [2-3]. Also as confirmed in recent papers accurate determination of water sorption correction for the silicon surface is one of the important factors in the framework of Avogadro project. In order to gain experiment and promote our data contribution to the kilogram redefinition work, the preliminary experiment was done at KRISS for adsorption effect on surface of 1 kg silicon sorption artifact (SA) [4] .The purpose of this investigation is to evaluate adsorption effect on surface of silicon sorption artifacts as a function of relative humidity and determine the coefficient of water vapor in moist air as well as the amount of water desorption from air to vacuum. For this purpose special 1 kg silicon artifacts in shape of cylinder and discs were fabricated at KRISS, which have about same mass and surface finish, material properties but very different surface area of 507.8 cm^2.The coefficient of water vapor adsorption in moist air and water vapor desorption from air to vacuum is to be determined using these special sorption artifacts.

2. MEASUREMENT PRINCIPLE

The objective of this investigation is to determine adsorption coefficient on 1 kg silicon artifacts in moist air as precisely as possible in range relative humidity of $0.07 < h < 0.73$. The gravimetric method was used as a main method for determining the adsorbed mass on surfaces of mass standard. It is based on comparison of two sorption artifacts having same mass, volume and same surface finish but very large difference in their surface areas assuming that adsorbed mass on surface of the silicon sample is proportional to its surface area. Therefore, the adsorbed mass per area can be given by

$$\mu = \frac{\Delta m_{air} - \Delta m_{vac}}{\Delta S} \qquad (1)$$

Where Δm_{air} , Δm_{vac} is the mass difference of two sorption artifacts in air and in vacuum respectively, ΔS is a surface area difference between two artifacts [4].

Adsorption of gas by solid is a result of attractive force of individual gas molecules with atoms of ions of solid. During the physical adsorption adsorbed molecules can be easily removed or desorbed by decreasing relative humidity of adsorption gas [5]. The physical adsorption analyzed quantitatively using model developed by Brunauer, Emmett and Teller (the BET model) which is employed following equation[6]:

$$\mu = \frac{\mu_m c_B h}{(1-h)(1+(c_B-1)h)} \qquad (2)$$

μ - is a quantity of adsorbed mass per area

c_B - is constant associated with adsorption energy.

μ_m - is quantity of adsorbed mass per area to produce monolayer. To obtain these parameters the BET equation is linearised by following:

$$\frac{h}{\mu(1-h)} = \frac{1}{c_B \cdot \mu_m} + \frac{c_B - 1}{c_B \cdot \mu_m} \cdot h \qquad (3)$$

and hereafter

$$intercept = \frac{1}{\mu_m \cdot c_B} \quad \text{and} \quad slope = \frac{c_B - 1}{\mu_m \cdot c_B}$$

Using these relations quantities of μ_m and c_B usually calculated [7]. The intercept of axis and slope is supposed to give useful information about the adsorption characteristics which depend on the physical state of surface and experimental conditions.

3. EXPERIMENTAL CONDITIONS

3.1 Instrumentation

Figure1 shows measurement system in our experiment. The measurement system consist of precise mass comparator (Mettler M_One), a vacuum pumping system, the humidity control unit and instruments for measuring the environmental conditions such as temperature, humidity, pressure. The mass comparator installed in vacuum chamber has capacity of 1 kg, readability of 0.1 μg with average standard deviation of 0.5 μg. The comparator equipped with automatic weight exchange mechanism for four mass standards. For evacuating the chamber oil free turbo molecular pump (Alcatel 5400CP, 400L/s) was used. Pressure inside the vacuum chamber could go down to 0.1 Pa in about 32 hours after the pump had been powered on.

3.2 Humidity control

For the generation of defined constant humidity a special humidity control unit is used as shown schematically in Figure 2. A dew-point meter (DM) directly connected to the flange of vacuum chamber. If desired concentration of water vapor is not high, one way is by letting air flow through water bath.

Figure 1.General view of experimental setup for humidity control

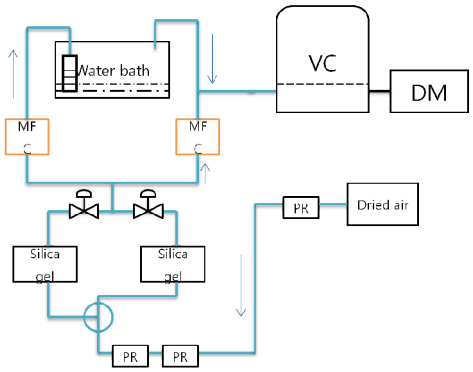

Figure 2. Schematic diagram of humidity controller DM-dew-point meter, MFC- mass flow controller, PR-pressure regulator , VC- vacuum chamber

In order to achieve very low humidity inside the vacuum chamber let the laboratory air flow through pressure regulator previously, and then dried by silica gel. The flow rate of either humid or dry air is adjusted by using manual valve of mass flow controller MFC. The maximum flow rate of adjustment is approximately 0.03/h for range of $h < 0.25$ and for $h > 0.6$ and 0.04/h for range of $0.25 < h < 0.6$. The humidity adjustment took place 1.5 hour to attain higher humidity inside the chamber whereas it took more than 10 hours to reach the very low humidity level. And it took more than 10 hours to get the equilibrium inside the chamber after the flow rate has been stopped from MFC humidity control unit.

To measure relative humidity during the comparison in the vacuum chamber a capacitive humidity sensor is used and this is calibrated against the dew-point meter. The sensors for measuring humidity, temperature and pressure the ambient conditions were installed near the samples inside the mass comparator.

3.3 Silicon sorption artifacts

In this experiment special sorption artifacts were employed: one is integral cylindrical artifact named as SA-C whose weight is approximately 1 kg, another named SA-D, and it consists of 6 pieces of discs and 18 pieces of small spacers. The total mass of these 6 discs adjusted close to mass of the cylindrical artifact. The small spacers of diameter 1 mm and height of 1.5 mm made of same material as SAs used to make gap between discs. As a result we made combination of silicon artifacts with mass differences about 9 mg with surface area difference 507.8 cm^2. Small mass difference between the samples can minimize the systematic effect caused by nonlinearity. The physical properties of SAs are given in Table 1. Also the silicon sphere artifact Si-Sphere (as density standard at KRISS) is included to confirm the mass difference between SA-D and SA-C. The heights and diameters were measured using three dimensional machine (ZEISS, UMM500) at the length laboratory of KRISS within the expanded uncertainty of 20 μm.

Table1. Properties of silicon artifacts and Si-Sphere

	SA-C /including spacers/	SA-D /including spacers/	Si-S
Mass (g)	999.841051	999.850128	999.838985
Height (mm)	89.388	97.1546	93.594
Diameter (mm)	79.5154(1)+13.43(1)+2(3)	79.51(4)+79.47(2)+2(18)+33.42(1)	93.594
Surface area (cm^2)	316.77	824,62	275.19
Volume (cm^3)	429.28	429.30	429.28
Surface roughness (R_z) , (μm)	0.026	0.026	
Purity (%)	99.999	99.999	

Figure 3. The 1kg silicon sorption artifacts used for sorption measurement: silicon sorption artifact-disc (SA-D) and silicon sorption artifact-cylinder (SA-C) and silicon sphere (Si-S)

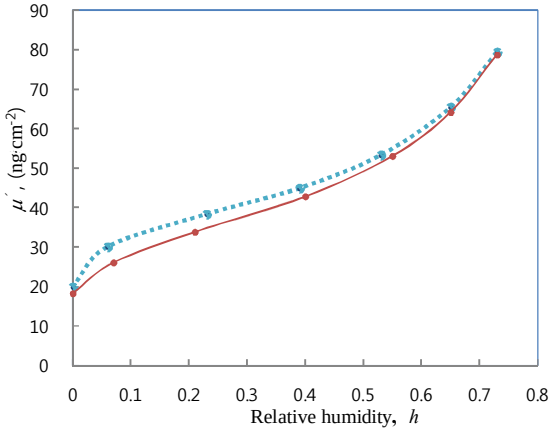

Figure 4. Adsorption isotherm (continuous line), of water vapor for silicon sorption artifacts SA-D and SA-C, (broken line desorption curve)

Surface area and volumes were calculated with reference to measured dimensions The surfaces are mirror polished the average surface roughness (R_z) is 0.0266 μm. The silicon artifacts and spacers were cleaned with purified methanol solvent for 30 min using ultrasound cleaning method, and then were dried.

4. MEASUREMENT PROTOCOL

The three series of mass comparison each consisting of 6 measurements of ABBA cycle were performed between the pairs of SA-D, SA-C and Si-S. The sorption measurement started after 49 days from the cleaning of the sorption artifacts had been taken. It took about 14 days for desorption and 12 days for adsorption measurement. The mean temperature during the whole measurement was (19.6±0.1) ^{0}C. The averaged standard deviation was 1.3 μg for adsorption measurement and 0.84 μg for desorption measurement. This value of standard deviation can be caused by the fact that comparatorôs door was removed to intensify the flow rate of dried air being reached the surface of SAs placed on the pans of mass comparator. In addition sensitivity of mass comparator was checked with built-in wire weight twice in the series at the beginning and at the end. Main source of measurement uncertainty was air buoyancy correction which is equal to the product of air density and the volume difference between two sorption artifacts compared.

The air density determined by the CIPM- 2007 equation with gas constant R=8.314472 J·mol^{-1}·K^{-1} and mole fraction of argon x_{Ar}=9.3315 mmol/mol. Standard deviation in vacuum has shown better than those in air.

5. RESULTS AND DISCUSSION

Figure 4 shows results obtained on the silicon sorption artifacts as an example between SA-D and SA-C which represent variation of adsorbed water layer as a function of relative air humidity. The continuous line represents adsorption isotherm which was determined by a least squares adjustment and each data point in the figure is average of 18 weighing results. As fitting function the BET equation (2) was used after correcting for long term drift after cleaning.

$$\mu' = \mu_0 + \frac{\mu_m c_B h}{(1-h)(1+(c_B-1)h)} \qquad (5)$$

Here, μ_0 designated the adsorbed mass per area at h=0. It differs from zero due to long term drift after cleaning or irreversible adsorption of water in conjunction with slight growth of oxide layer [8]. Due to the observed increase in amount of adsorbed mass at low humidity range (h < 0.1) irreversible adsorbed mass per area estimated as μ_0=0.018 μg/cm^2 for adsorption, μ_0=0.020 μg/cm^2 for desorption isotherm respectively with combined

Table 2. Summary of measurement data between SA pairs

Sorption artifacts SAs	Monolayer capacity μ_m (ng·cm^{-2})	Standard uncertainty $u(\mu_m)$ (ng cm^{-2})	Adsorption coefficient $\delta\mu/\delta h$ (ng·cm^{-2}·%$^{-1}$)	Standard uncertainty $u(d\mu/dh)$ (ng·cm^{-2})	Surface area difference (cm^2)
SA-D and SA-C	17	1.8	65.3	8.2	507.8
SA-D and Si-S	44.5	2.2	145	6.25	549.42
SA-C and Si-S	412	17	1515	207.2	41.58

standard uncertainty of 0.008 μg·cm^{-2}. From the adsorption curve we calculated μ_m=0.017 μg/cm^2 monolayer capacity with estimated standard uncertainty of 0.0018 μg/cm^2 (k=1) and the BET constant c_B=9.3±1.6. For these calculations we utilized data obtained at relative humidity in the range from 0.23 < h < 0.53. Since the energy constant c_B is greater than 1 and S-shaped curve in figure 4 shows that adsorption isotherm for water vapor on silicon surfaces corresponds to type II according to BET classification. It is likely that multilayer adsorption take place on the silicon surface. The adsorption coefficient $\delta\mu/\delta h$ gives the amount of adsorbed water layer per unit of relative humidity. Taking the approximate slope of the μ value in limited humidity range 0.3 < h < 0.6 we find that

$$\frac{\delta\mu}{\delta h} = (65.3 \pm 8.2) \ \text{ng·cm}^{-2}\text{·\%}^{-1}$$

From this coefficient amount of adsorbed mass on silicon sphere with surface area of 275 cm^2 in moist air (h=0.5) deduced as of 13.75 μg. Comparing with other studies, our results are same order of magnitude as: μ_m=0.017 μg/cm^2, c_B=5 and $\delta\mu/\delta h$=100 ng·cm^{-2}·%$^{-1}$, reversible adsorbed water vapor as of 8.2 μg in the reference 7 and μ_m=0.028 μg/cm^2 in the reference 9.

In addition we have measured adsorption isotherm for the pairs of SA-D and Si-S and SA-C and Si-S. Table.2 summarizes the results of these measurements. As shown in the table first two cases are comparable because of similar surface area difference between the pairs of SA-D and SA-C and between SA-D and Si-S, however comparison the SA-C with Si-S gives unreasonable values due to the small difference in their surface area. For the second case adsorption coefficient is higher than that of first one which is probably due to surface quality and difference in shape between SA-D and Si-S. It can be concluded that for accurate evaluation of the sorption effect by gravimetric method, surface area difference between sorption artifacts must be large enough and sorption artifacts have uniform surface polishing, roughness.

6. CONCLUTION

The adsorption isotherm experimentally obtained on the surface of silicon sorption artifacts at various relative humidity range of 0.07 < h < 0.73 using the pair of 1 kg special silicon sorption artifacts producing effective surface area and mass difference. The sorption behavior of silicon SAs corresponds to type II, according to which the physical adsorption and multilayer formation on the silicon surface can be explained. From obtained BET parameters μ_m=0.017 μg/cm^2, c_B=9.3 approximate slope for the mass change due to the adsorption effect was calculated as $\delta\mu/\delta h$=65.3 ng·cm^{-2}·%$^{-1}$. We observe the increase of mass difference between SAs in low humidity range which could be explained due to the dissociative adsorption of water molecules on silicon surface.

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