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DENSITY MEASUREMENT OF A THIN-FILM BY THE PRESSURE-OF-FLOTATION METHOD

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Abstract: A method for density and thickness measurements of a thin-film is described by the pressure-of-flotation method (PFM). The density and thickness of a silicon thermal oxide layer on silicon crystal are determined by measuring the density and mass differences for the sample with and without the thin-film. Details on the density and thickness measurement and the results of the measurements are presented.

Keywords: density, pressure-of-flotation, thin-film, molybdenum, silicon oxide.

1. INTRODUCTION

Silicon single crystals are used as density standards and for a determination of the Avogadro constant, N_A [1, 2]. The N_A value is determined by absolute measurements of lattice constant a, density ρ and mean molar mass M of silicon single crystals from a following formula:

$$N_A = \frac{8(M/\rho)}{a^3} = \frac{M/\rho}{8^{1/2} d_{220}^3} , \qquad (1)$$

where d_{220} is (220) silicon lattice spacing. Absolute density of silicon crystals is measured by optical interferometry and mass measurements, while very small density difference of silicon crystals can be measured by pressure-of-flotation method (PFM) [3]. Recently a new pressure-of-flotation (PF) apparatus was installed at NMIJ to investigate the density of silicon crystals [4, 5]. The new PF apparatus consists of a vacuum-insulated water bath and has an estimated relative standard uncertainty of 4×10^{7} [6].

The PFM is used to evaluate homogeneity of silicon ingots as well as to study defects of silicon crystals. Moreover surface characterization such as an oxide layer on the silicon crystal is also important for the determination of N_A. In this paper, the PFM is applied to the measurement on density and thickness of a SiO_2 thin-film on a silicon substrate, which provides a new method to measure the density and thickness of a thin-film.

2. PRESSURE-OF-FLOTATION METHOD

Fig. 1 shows a schematic diagram of the PFM. Two silicon samples are put in the sample container with a liquid mixture of 1,2,3-tribromopropane and 1,2-dibromoethane. In

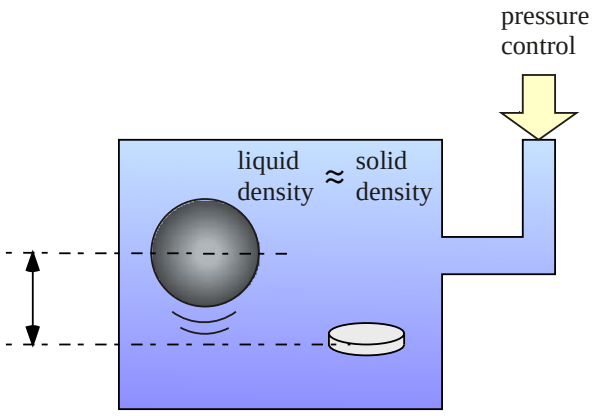

Fig. 1. Schematic diagram of the PFM

the PF measurement, additional pressure is applied to change the density of the working liquid. When the liquid density becomes equal to that of a solid sample, the solid sample floats in the liquid. We call the pressure when the sample floats in the liquid flotation pressure. The relative density difference between two silicon samples 'Si, 1' and 'Si, 2' is calculated from the difference between the flotation pressure p_1 and p_2 as

$$\frac{\Delta\rho}{\rho} = \frac{\rho_{Si,2} - \rho_{Si,1}}{\rho_{Si,1}} = (\kappa_{liq} - \kappa_{Si})(p_2 - p_1) , \qquad (2)$$

where κ_{liq} and κ_{Si} are the isothermal compressibilities of liquid and silicon, respectively. Determination of effective compressibility $\kappa_{liq} - \kappa_{Si}$ is very important to achieve more accurate density comparison measurements, which was demonstrated in the previous paper [5, 6].

Fig. 2 shows our PF apparatus at NMIJ. The thermostat has a vacuum insulation from the surroundings and temperature-regulated water circulates around this vacuum insulation. The temperature of the water in the bath is measured by a platinum-resistance thermometer and a dc resistance bridge. Temperature of the bath is controlled by a PID algorithm. The pressure inside the glass vessel is controlled and stabilized to be constant within ± 0.01 kPa by a manometer and a pneumatic pressure controller connected via a Teflon tube. Sample movement is observed by using a CCD camera and a monitor. The CCD camera is mounted on the x-z stage with a linear scale. In order to keep the

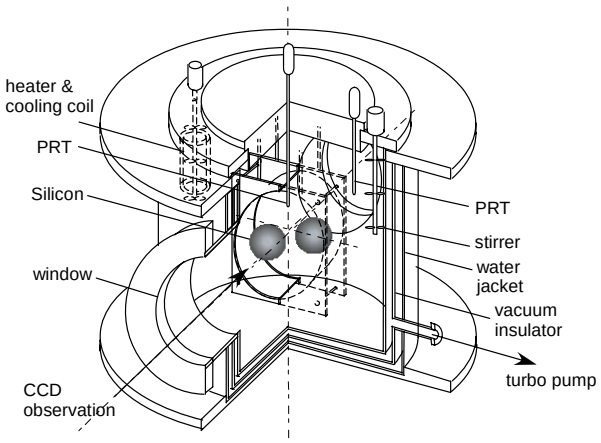

Fig. 2. Schematic diagram of the PF apparatus at NMIJ

amount of heat absorption small and to prevent photolysis of bromoderivatives, the measurement is carried out in a dark room.

3. DENSITY MEASUREMENT FOR A THIN-FILM

The PFM is used for density comparison measurements between bulk silicon crystals. A new application of the PFM is recently developed [7]. By measuring the density and mass differences for the sample with and without a thin-film, the density and thickness of the thin-film can be determined. Since the PFM can measure very small density differences between samples, it can be applied to measure density and thickness of a thin-film on a silicon substrate (Fig. 3). A density difference $\Delta\rho/\rho_0$ is determined by the PFM while a mass difference is measured by an electric balance for the samples before and after thin-film is prepared on a substrate. Then the density ρ_X of the thin-film on the substrate can be derived as follows:

$$\rho_X = \rho_0 \left(1 - \frac{1 + m/\Delta m}{1 + \rho_0/\Delta\rho} \right)^{-1} , \qquad (3)$$

where m and Δm are masses of the substrate and the thin-film, respectively. Then thickness of the thin-film can be obtained as

$$\Delta t = \frac{\Delta m}{S\rho_X} , \qquad (4)$$

where S is a surface area of the substrate on which thin-film is prepared. Since the measurement techniques used here are all macroscopic ones, only average density and thickness of the thin-film can be determined. This method directly measures the density of a thin-film.

4. EXPERIMENTAL PROCEDURE

The density difference between a silicon substrate and a reference silicon sample is measured by the pressure-of-flotation apparatus. The mass difference between the substrate and the reference is also measured by an electric balance, where air temperature and air pressure are monitored in order to calibrate the air density contribution. The balance has a weight exchange mechanism, and all mass measurements are automatically controlled by the

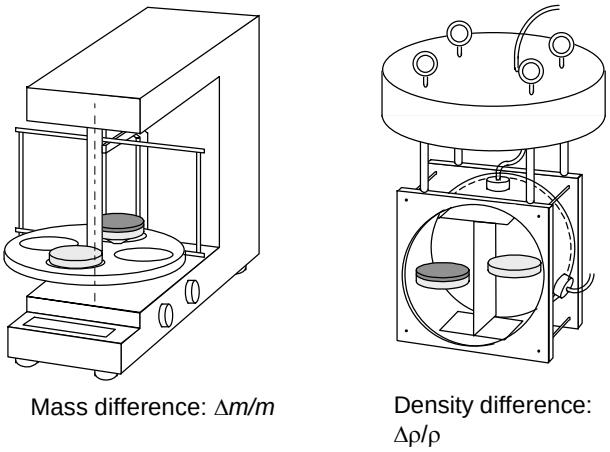

Fig. 3. Measurement on density and thickness for a thin-film on a silicon substrate.

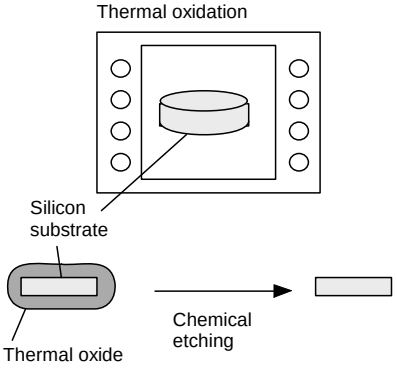

Fig. 4. Density measurement procedure for thermal silicon oxide on the silicon substrate.

computer. The balance sensitivity determined in the measurement for the 1 kg silicon sphere is used in this paper. Density and mass difference between the sample and the reference are measured again after thin-film is prepared. Here it is assumed that thin-film does not soak up working liquid in the PF experiment. Finally density difference $\Delta\rho/\rho_0$ and mass difference $\Delta m/m$ are calculated and then the density of the thin-film is derived as described in section 3. The surface area of a substrate where a thin-film is prepared can easily be measured, and average thickness of the thin-film is calculated.

Silicon substrates (dimensions: ϕ50 mm × 5 mm, ρ = 2329 kg/m^3) were cut from a Cz-silicon single crystal. Thermal oxide layer was grown by heat treatment (thermal oxidation). Because silicon atoms of the oxide layer are supplied from silicon substrate during oxidation, mass of the oxide layer cannot be determined from mass comparison measurement before and after thermal oxidation. Therefore experimental procedure was arranged as shown in Fig. 4. At first thermal oxidation was carried out by annealing. After measuring the density and mass differences as compared

Table 1. Flotation Pressure and Mass Difference for the sample with and without the SiO_2 layer. Density and thickness of SiO_2 layer are calculated from equation (3) and (4).

Quantity	Symbol	Value	Relative standard uncertainty
Relative density difference	$\Delta\rho/\rho$	$(2.73 \pm 0.08) \times 10^{-6}$	
Relative mass difference	$\Delta m/m$	$(-71.8 \pm 1.8) \times 10^{-6}$	
Surface area	S	(47.12 ± 0.91) cm^2	
Density of thermal oxide layer	ρ_X	(2244 ± 2) kg m^{-3}	0.1 %
Thickness of thermal oxide layer	Δt	(157.4 ± 5.1) nm	3.2 %

with the reference silicon sample, thermal oxide layer was removed by chemical etching. The density and mass difference were measured after etching. Finally, the density of the silicon thermal oxide layer can be evaluated.

5. RESULTS AND DISCUSSION

Table 1 summarizes result for density measurement of silicon oxide layer. The density of the SiO_2 layer with the standard uncertainty is derived to be (2244 ± 2) kg/m^3 from (3). Relative uncertainty of the density is about 0.1 % in this experiment. Then average thickness of the thin-film is estimated to be (157.4 ± 5.1) nm. The density of bulk thermal oxide is 2270 kg/m^3, and the density of a SiO_2 thin-film prepared by thermal oxidation is almost the same of that of the bulk SiO_2. Further investigation of the silicon thermal oxide on the silicon crystals is now in progress.

In the previous paper, density and thickness measurements of a molybdenum thin film on the silicon substrate were demonstrated by this method [7]. The standard relative uncertainty of the density of the molybdenum thin-film was large (about several %), which is mainly due to the large density difference between the molybdenum thin-film and the silicon substrate. Because density of the Mo is about 4 times as large as that of the silicon crystals, very small amount of the Mo thin-film causes large density change of the sample. The PFM is very precise measurement and the measurement range of our PF apparatus is 15×10^{-6} in relative density, which makes the measurement for the Mo thin-film difficult. The density of the thermal oxide is close to that of the silicon crystal, therefore, more accurate density measurement of a thin-film is possible.

6. CONCLUSION

The density and thickness measurement of a thin film was described. A thermal oxide layer was prepared by thermal oxidation technique on the silicon substrate. Density and thickness of the thermal oxide layer on the silicon substrate were determined.

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