Measurement on Compressibility Coefficient for Density Standard Liquid at 2329 kg/m^3

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Abstract: The accurate measurement on the compressibility coefficient of density standard liquid at 2329kg/m^3 (DSL-2329) plays an important role in the quality control for silicon single crystal manufacturing. A new method is developed based on hydrostatic suspension principle in order to determine the coefficient with high measurement accuracy. Two silicon single crystal samples with known density are immersed into a sealed vessel full of DSL-2329. The density of liquid is adjusted with varying liquid temperature and static pressure, so that the hydrostatic suspension of two silicon single crystal samples is achieved. The compression coefficient then calculated by using the data of temperature and static pressure at the suspension state. One silicon single crystal sample can be suspended at different state, as long as the liquid temperature and static pressure function linearly according to a certain mathematical relationship. By using the method based on hydrostatic suspension principle, the compressibility coefficient can be measured at the same time, and measurement precision can be improved due to avoiding the influence of liquid surface tension. This method was further validated experimentally, where the mixture of 1, 2, 3-tribromopropane and 1,2-dibromoethane is used as DSL-2329. The compressibility coefficient was measured, as 5.4×10^{-10} Pa^{-1}.

Keywords: silicon single crystal sample, hydrostatic suspension, density standard liquid at 2329kg/m3, compressibility coefficient measurement.

1. INTRODUCTION

As one import part of crystals, silicon single crystal(SSC) is widely used for semi conducting materials, power generation and heat supply based on photovoltaic converter. Performance of semi conducting device is influenced by the purity and homogeneity of SSC[1–2].With the development of integrated semi conducting industry, especially large scale integrated circuit(LSIC) and quantum computer, requirements on the purity and homogeneity for SSC is higher and higher. Preparation of high-purity SSC has become one of the key technologies in IC industry with the purity requirement up to 99.999 9%, even higher than 99.999 999 9%[3–4].To increase wafer yield and stability, accurate measurement of purity and homogeneity of SSC has become a key research issue. As an important physical parameter of SSC materials, density not only indicates material molecular arrangement inside SSC, but also is the external expression of the structure and composition for the internal composition. Density measurement for SSC has therefore become one important solution for high-precision quality control of SSC manufacturing[4–7], with the requirement of relative measurement accuracy up to 1×10–6. To ensure measurement accuracy, SSC material should be placed in density standard liquid at 2329 kg/m3(DSL-2329). Uniformity of the measurement environment can be maintained due to the fact that 2329 kg/m3 approaches the density of SSC. However, there is significant difference in thermodynamic characteristics between DSL-2329 and SSC, particularly in terms of compressibility coefficient. These parameters are main factors which influence the measurement accuracy of SSC density [8–10]. Hence, it is important to precisely measure the compressibility coefficient of DSL-2329.

There mainly exist three methods for compressibility coefficient measurement:

(1) Definition Method. By applying pressure to DSL-2329 with a certain volume, the pressure-volume curve can be obtained; the compressibility coefficient can be then calculated according to its definition. As a direct measurement, this method shows its advantage for simple use and easy automation[11–17].

(2) Sonic velocity method. According to the sonic longitudinal wave propagation equation in liquid and plane wave propagation equation in ideal medium, the functional relationship can be established between the sonic velocity and compressibility coefficient of DSL-2329; the compressibility coefficient can be solved if the sonic speed is measured. However, the measurement accuracy of compressibility coefficient is limited due to indirect measurement[18–22].

(3) Cross-correlation method. According to the cross correlation calculation between two pressure signals from sensors installed in one pipeline, the signal transfer time can be obtained, then by using the mathematical model covering the sonic velocity, compressibility coefficient and density mentioned in the sonic velocity method, the compressibility coefficient can be calculated[23–25]. Compared with sonic velocity method, cross-correlation method does not require the mutation of pressure in the pipeline, which can accurately measure the signal transfer time. However, the measurement system is relatively complex, as an indirect measurement. Repeatability in the low and medium pressure range is not good enough. The test range is widest among the three existing measurement methods mentioned above. Compressibility curve is usually obtained by the fitting

method due to less sampled data, particularly in the low pressure range used for SSC materials measurement.

On the other hand, temperature fluctuations due to Joule-Thomson effect during liquid compression does not satisfy the requirement on constant temperature for SSC material measurement. Furthermore, the measurement accuracy within low pressure rang should be improved.

Near ten international member laboratories of International Avogadro Comminute(IAC) have made joint efforts and achieved high-precise measurement on the compressibility coefficient for silicon single crystal sample[27–33], $7.68 \times 10^{-6} \mathrm{K}^{-1}$ and $1.022 \times 10^{-11} \mathrm{Pa}^{-1}$ respectively. Based on these two standard data, a new measurement method for compressibility expansion coefficient of DSL-2329 is developed. Two silicon single crystal samples with known density, compressibility and coefficient was immersed into DSL-2329, and brought into suspension state by adjusting the liquid temperature and pressure. According to liquid the temperature and pressure in the suspension state, compressibility coefficient of DSL-2329 could be solved based on a mathematical model. An experimental system was designed to validate the measurement principle. Compressibility coefficient of DSL-2329 made of tribromopropane(1, 2, 3-tribromopropane) and dibromo- ethane (1, 2-dibromoethane) was measured.

2. PRINCIPLE FOR MEASUREMENTS ON COMPRESSIBILITY COEFFICIENT OF DSL-2329 BASED ON HYDROSTATIC SUSPENSION METHOD

According to thermophysical characteristics of liquid, there is mathematical relationship among homogenous liquid density ρ_L, temperature t and pressure p acting on the liquid, provided that component proportion in liquid is not changed within short time[34–37]:

$$\rho_L(t, p) = \rho_L(t_0, p_0)[1 - \gamma_L \times (t - t_0) + K_L \times (p - p_0)] \quad (1)$$

where $\rho_L(t_0, p_0)$ is the liquid density at reference temperature t_0 and pressure p_0, $t_0 = 20°C$, $p_0 = 101\,325$ Pa; γ_L is thermal expansion coefficient of liquid, K^{-1}; K_L is compressibility coefficient of liquid, Pa^{-1}.

Similarly, if the internal crystal structure of SSC does not change in short time. A mathematical model including density ρ_{Si}, temperature t and pressure p can be described as

$$\rho_{Si}(t, p) = \rho_{Si}(t_0, p_0)[1 - \gamma_{Si} \times (t - t_0) + K_{Si} \times (p - p_0)] \quad (2)$$

where $\rho_{Si}(t_0, p_0)$ is the SSC density at reference temperature t_0 and pressure p_0, $t_0 = 20°C$, $p_0 = 101\,325$ Pa; γ_{Si} is thermal expansion coefficient of SSC, K^{-1}; K_{Si} is compressibility coefficient of SSC, Pa^{-1}.

Two SSC samples S_1 and S_2 with known K_{si} and γ_{si} are immersed into a sealed vessel containing DSL-2329, which is mounted in a thermostat water bath, shown in Fig. 1.
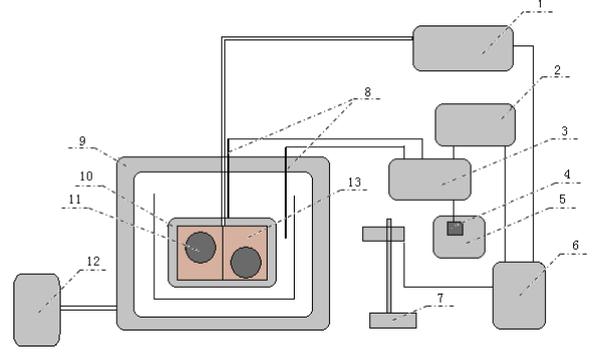

Fig. 1. Principle of hydrostatic suspension of silicon single crystal sample

Based on the thermodynamic characteristics and compressibility of liquid, the liquid density can be changed by adjusting its temperature and pressure. Static force balance and stable suspension of two samples S_1 and S_2 can then be achieved at (t_1, p_1) and (t_2, p_2) respectively, if the following equations are satisfied:

$$\rho_{Si1}(t_1, p_1) = \rho_L(t_1, p_1) \quad (3)$$

$$\rho_{Si2}(t_2, p_2) = \rho_L(t_2, p_2) \quad (4)$$

By combining Eq. (1)–Eq. (4), the density difference between two samples S_1 and S_2 at reference temperature and pressure can be expressed as follows:

$$\frac{\Delta\rho}{\rho} = \frac{\rho_{Si1}(t_0, p_0) - \rho_{Si2}(t_0, p_0)}{\rho_{Si1}(t_0, p_0)} = 1 - \frac{[1 - \gamma_L \Delta t_2 + K_L \Delta p_2][1 - \gamma_{Si} \Delta t_1 + K_{Si} \Delta p_1]}{[1 - \gamma_L \Delta t_1 + K_L \Delta p_1][1 - \gamma_{Si} \Delta t_2 + K_{Si} \Delta p_2]} \quad (5)$$

where $\Delta t_1 = t_1 - t_0$, $\Delta t_2 = t_2 - t_0$, $\Delta p_1 = p_1 - p_0$, $\Delta p_2 = p_2 - p_0$.

Mathematical model Eq. (5) indicates that density difference is a function of floatation temperature, pressure at the sample center, compressibility and thermal expansion coefficients of DSL-2329. If high order items are neglected, Eq. (6) can be derived from Eq. (5):

$$\frac{\Delta\rho}{\rho} = -(\gamma_l - \gamma_{si}) \times (t_2 - t_1) + (K_l - K_{si}) \times (p_2 - p_1) \quad (6)$$

For a SSC sample, such as S_1, there exists (t_{11}, p_{11}) and (t_{12}, p_{12}) at which sample S_1 can be floated. Since the same SSC sample is used, the following equations are satisfied:

$$K_{Si} \ll K_L, \gamma_{Si} \ll \gamma_L.$$

then

$$\Delta\rho = 0$$

Eq. (6) can be tranformed into

$$0 = -(\gamma_l - \gamma_{si}) \times (t_{12} - t_{11}) + (K_l - K_{si}) \times (p_{12} - p_{11}), \quad (7)$$

Based on Eq. (5) and Eq. (7), the mathematical model for K_L and γ_L can be deduced as

$$\begin{cases} K_l = \dfrac{(t_{12} - t_{11})\Delta\rho}{[(t_1 - t_2)(p_{12} - p_{11}) - (p_2 - p_1)(t_{12} - t_{11})]\rho} + K_{si} \\ \gamma_l = \dfrac{(p_2 - p_1)\Delta\rho}{[(-t_2 + t_1)(p_{11} - p_{12}) + (t_{11} - t_{12})(p_2 - p_1)]\rho} + \gamma_{si} \end{cases} \quad (8)$$

Three advantages feature for this measurement method:

(1) By using non-contact phase shift interferometry system, the relative measurement accuracy for $\Delta\rho$ and ρ of two SSC samples can reach 2×10^{-7}. Similarly, temperature t and pressure p can be measured with resolution $10\,\mu K$ and $1\,Pa$ by high-resolution devices. Hence, all the parameters used in mathematical model (8) can be measured with enough precision to ensure the accuracy for K_L and γ_L.

(2) The measurement error due to liquid surface tension is avoided by applying this hydrostatic suspension principle because there are not moving parts on the liquid surface.

(3) Since the density of SSC sample is very close to that of DSL-2329, the flotation of silicon sample can be achieved by adjusting pressure within low pressure range. It ensures precise measurement for K_L and γ_L in the low pressure range, and reduces temperature fluctuation due to Joule-Thomson effect.

3. EXPERIMENTAL SYSTEM DESIGN AND DATA ANALYSIS

According to the schematic diagram shown in Fig. 1, an experimental system based on hydrostatic suspension principle is designed. 1, 2, 3-tribromopropane ($2410\,kg/m^3$ at $20\,℃$) and 1, 2-dibromoethane($2180\,kg/m^3$ at $20\,℃$) are mixed in accordance with certain proportion to achieve a homogenous DSL-2329. Its density was calibrated by a high-precision oscillating tube density meter from time to time.

It is shown in Eq. (5) that the vaster the density difference between two SSC samples, the greater the discrepancy of temperature and pressure at which silicon sample floats. Therefore, to achieve better measurement, two SSC samples with large density difference were chosen, as $Si_{\_max}$ and $Si_{\_min}$. By using non-contact phase shifting interferometry system and high-precision electrical mass comparator, the density difference of $0.014836\ kg/m^3$ between two samples was detected. The two SSC samples were slowly placed into a vessel containing DSL-2329 to ensure that there is no air bubble generated on the surface of SSC samples. Afterwards, the vessel was sealed and installed in a thermostat water bath.

Compared with pressure, density of DSL-2329 is more sensitive to temperature. Therefore temperature control accuracy of thermostat water bath is a key factor to ensure the validity for the whole measurement system. PID algorithm was applied for temperature control for the thermostat water bath. The temperature-time curve of liquid is shown in Fig. 2.

Fig. 2 illustrates that the liquid temperature t can be controlled with maximum error $50\,\mu K$ within $5\,h$. The standard deviation is $29\,\mu K$ if t obeys uniform distribution. The relative error of density measurement due to liquid temperature fluctuation is $\pm4\times10^{-8}$ according to Eq. (6). Temperatures along different directions in the vessel were

measured. It showed that the temperature distribution around the vessel was homogenous with maximal deviation $0.1\,mK$.
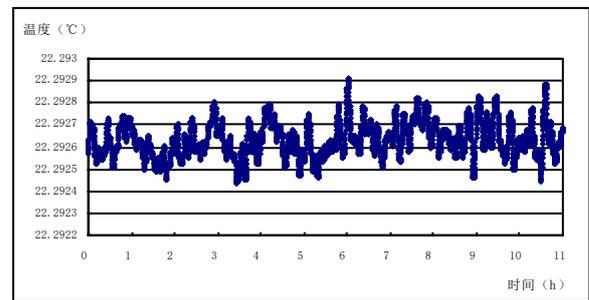

Fig. 2. Temperature-time curve for thermostat water bath

To avoid impact on to liquid temperature due to lights, all the lights in the room were turned off during measurement. Liquid temperature was measured by using electric bridge(relative resolution 1×10^{-9}) and primary standard platinum-resistance thermocouple (resolution $1\,\mu K$). According to theoretical calculation, even the heating effects of platinum resistance can cause liquid temperature change about $1\,mK$. The primary standard platinum-resistance thermocouple was therefore installed in one place out of liquid but close to the middle of vessel.

Firstly, the pressure was kept constant. The liquid temperature was scanned by step $1\,mK$ to seek approximate values at which two silicon samples are floated respectively. The fact is that the temperature change in thermostat water bath and vessel containing DSL-2329 and silicon samples were not synchronized with one time constant $\tau=20\,min$. Therefore, three time constants(about one hour) should be waited for the temperature uniformity if the temperature of liquid was changed. The critical values of temperature for $Si_{\_max}$ and $Si_{\_min}$ was $22.364\,℃$.

During measurement SSC sample $Si_{\_min}$ was near force-balance state and moved slowly along vertical direction. Fine adjustment for liquid density was carried out by the pressure PID control system to change the buoyancy acting on the SSC sample $Si_{\_min}$. The pressure adjustment was achieved by changing the height of a smaller vessel connected to the measurement container via tube. The feedback information for pressure control included velocity and displacement of silicon sample center along the vertical direction, which were calculated based on image analysis and real-time iterative algorithm. The target of pressure control system is to keep silicon sample $Si_{\_min}$ stable within $\pm100\,\mu m$ along vertical direction in $10\,min$, which was regarded as balanced state. The resolution of CCD image analysis system is $10\ \mu m$, which corresponds to density measurement relative error $\pm1\times10^{-8}$. The pressure regulation was relatively smaller than other methods mentioned above, which reduced the impact on liquid temperature fluctuation

due to Joule-Thomson effect.

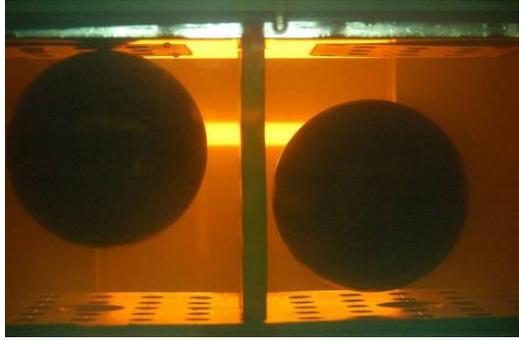SSC sample Si$_{\_min}$ at hydrostatic suspension state is shown in Fig. 3.

Fig. 3. Silicon sample Si$_{\_min}$ at hydrostatic suspension state(the left one is Si$_{\_min}$, and the right one is Si$_{\_max}$)

To avoid influence of current due to other silicon sample, silicon sample Si$_{\_max}$ was fixed by magnetic-couple devices when SSC sample Si$_{\_min}$ was being measured, and vice versa. Temperature t_1, pressure p_1 and height of silicon sample center h_1 were measured for SSC sample Si$_{\_min}$.

Eq. (7) indicats that one SSC sample, for example Si$_{\_min}$, can be floated stably if the temperature t and pressure p comply with Eq. (9):

$$\frac{t_{11}-t_{12}}{p_{11}-p_{12}}=\frac{K_l-K_{si}}{\gamma_l-\gamma_{si}}=c \qquad (9)$$

According to mathematical model above, two groups of temperature t and pressure p, at which hydrostatic suspension of SSC sample can be achieved, are enough for calculation of constant c. To ensure accuracy, four groups of temperature t and pressure p were measured for SSC sample Si$_{\_min}$, shown in Fig. 4.

By using least square algorithm, the constant c is calculated:
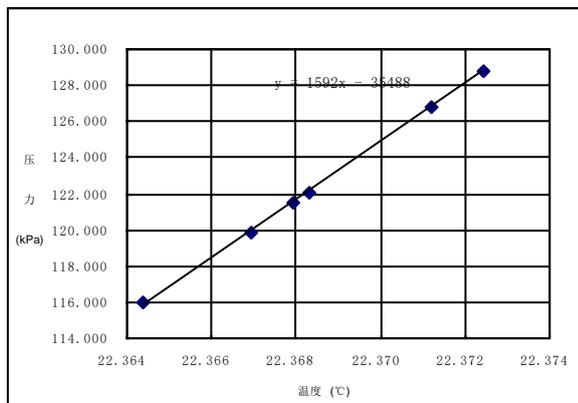
$$c=1592.0 \text{ kPa}/℃.$$

Fig. 4. Experimental data of temperature and pressure at hydrostatic suspension state for silicon sample Si$_{\_min}$

Based on Eq. (8), known density of two silicon samples and all measured data of temperature and pressure, the compressibility coefficient of DSL-2329 were calculated:

$$K_L=5.4\times10^{-10}\,\text{Pa}^{-1}.$$

4. CONCLUSIONS

(1) By regulating liquid temperature and pressure, density of DSL-2329 can be adjusted finely, and then hydrostatic suspension of SSC sample in DSL-2329 can be achieved.

(2) One silicon sample can be floated stably at different liquid temperature t and pressure p if t and p comply with certain linear mathematical model. By immersing two SSC samples with known density, compressibility and thermal expansion coefficients into one sealed vessel full of DSL-2329, the compressibility and thermal expansion coefficients of DSL-2329 can be solved if temperature and pressure at hydrostatic suspension state are measured.

(3) One experimental system based on hydrostatic suspension principle is designed, and liquid temperature can be controlled with maximal deviation $50\,\mu$K within 5 h. The hydrostatic suspension of silicon sample can be achieved by PID pressure control system. The mixture of 1,2,3-tribromopropane and 1,2-dibromoethane was used as DSL-2329. The compressibility and thermal expansion coefficients were measured, and values were 8.5×10^{-4} K^{-1} and 5.4×10^{-10}Pa^{-1} respectively, which validated effectiveness of the measurement method and experimental system.

(4) By applying this hydrostatic suspension principle, measurement error due to liquid surface tension in Mattiessen method is avoided. As one reference measurement method, the high-precision measurement for compressibility and thermal expansion coefficients of DSL-2329 can be achieved within low pressure range, which reduced liquid temperature fluctuation due to Joule-Thomson effect.

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