Real Time Evaluation of Silicon Epitaxial Growth Process by Exhaust Gas Measurement Using Quartz Crystal Microbalance

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A silicon epitaxial growth process in a trichlorosilane-hydrogen system was evaluated using a quartz crystal microbalance (QCM) placed at the exhaust of a chemical vapor deposition reactor designed for the Minimal Fab. The QCM showed two types of the frequency decrease behaviors, that is, *i*) a quick shift due to the gas property change caused by the trichlorosilane gas introduction into the ambient hydrogen and *ii*) the continuous and gradual decrease due to the byproduct deposition on the QCM surface during the silicon epitaxial growth. Because both *i*) and *ii*) showed a relationship with the silicon epitaxial growth rate, the *in-situ* information obtained by the QCM was expected for the real time monitoring of the film deposition process.

1. Introduction

Silicon epitaxial growth has a long history [1, 2] in the electronics industry. Its industrial processes use chlorosilane gases, such as trichlorosilane ($SiHCl_3$) and dichlorosilane (SiH_2Cl_2) [3-5]. The produced films are uniform and flat at the atomic level and the growth rate is quite high.

Due to its reasonable cost and ease of use, the trichlorosilane gas has been very often used. The trichlorosilane gas, having the boiling point of 31 ^{o}C, is produced by the bubbling technique, *i. e.*, injecting hydrogen gas into the liquid trichlorosilane contained in a cylinder. In a mass-production plant having many epitaxial reactors for large diameter wafers, a huge amount of the trichlorosilane and hydrogen gas mixture is produced at the precisely controlled concentration and is supplied from a large tank to the reactors *via* tube networks. In contrast, in very small equipment, such as the Minimal Fab [6, 7] using small wafers of a half-inch diameter, the gas supply condition is quite different from the mass-production plant. The compact-designed Minimal chemical vapor deposition (CVD) reactor [8-10] consumes significantly small amounts of the precursors in a short time period, for example, the trichlorosilane gas at the flow rate of 10-20 sccm at atmospheric pressure for a few minutes. In order to finely control the trichlorosilane gas concentration at the significantly low gas flow rate, any *in situ* real time measurement method is helpful. Additionally, the measured information is expected to show the relationship with the epitaxial growth rate.

For this purpose, a piezoelectric crystal microbalance, such as a quartz crystal microbalance (QCM) and a langasite crystal microbalance [11-18], may be a candidate, because it

can sensitively detect the significantly weak signals such as the change in the gas properties and the increase in the nano-gram-level weight of the thin film formed at the surface. Previous studies [14-17] have reported that the deposition of the byproducts of $(SiCl_2)_n$, from the trichlorosilane gas could be *in situ* measured by the QCM. The byproduct formation and deposition measured by such sensors should be evaluated as to whether they have a relationship with the epitaxial growth rate. Such the relationship will help developing and controlling the epitaxial growth process.

In this study, the QCM was used to measure the exhaust gas of the silicon epitaxial reactor designed for the Minimal Fab. The typical QCM frequency changes were, for the first time, classified and evaluated for obtaining the *in-situ* real time information of the epitaxial growth process.

2. Experimental procedure

Figure 1 shows the Minimal CVD reactor and the QCM system. This reactor consists of a half-inch silicon wafer (12.5-mm diameter and 0.25-mm thick), a transparent quartz tube, a wafer holder made of quartz glass, a gas inlet and three heating units consisting of a halogen lamp and a reflector. The inner diameter of the quartz tube is 24 mm. The wafer holder diameter is 19 mm. The wafer is rotated at the rate of 0 - 30 rpm. The infrared light emitted from the halogen lamps for the heating is concentrated on the half-inch wafer surface. The quartz tube wall is cooled from the outside by flowing air [6] in order to maintain the cold wall environment.

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The precursor gas and the carrier gas, trichlorosilane and hydrogen, respectively, are introduced at atmospheric pressure from the top of the reactor through the gas inlet. The hydrogen gas flow rate was 85 sccm, a part of which was divided and injected into the liquid trichlorosilane cylinder for the bubbling and for producing the gas mixture of trichlorosilane and hydrogen. The trichlorosilane gas of typically 21 sccm at 25 °C was produced by the hydrogen gas at the flow rate of 35 sccm, based on the trichlorosilane vapor pressure [19]. The total gas flow rate was typically 106 sccm. The trichlorosilane gas concentration significantly depends on the liquid temperature.

The trichlorosilane gas causes the surface reactions based on equations (1) and (2). The symbol * indicates the species chemisorbed at the surface. The rate equation [20] is written as equation (3) following the Eley-Rideal model.

$$SiHCl_3 \rightarrow {}^*SiCl_2 + HCl. \tag{1}$$

$$^*SiCl_2 + H_2 \rightarrow {}^*Si + 2HCl. \tag{2}$$
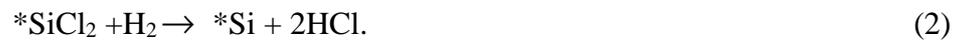
$$R_{Si} = \frac{k_{ad}k_r[SiHCl_3][H_2]}{k_{ad}[SiHCl_3] + k_r[H_2]}. \tag{3}$$

R_{Si} is the silicon epitaxial growth rate. $[i]$ is the concentration of species i at the wafer surface. k_{ad} and k_r are the rate constants of equations (1) and (2), respectively.

A significantly small amount of *SiCl$_2$ desorbs from the silicon surface into the gas phase for producing SiCl$_2$, following equation (4) [17]. Even in the cold wall environment, the trichlorosilane gas produces a significantly small amount of SiCl$_2$ by thermal decomposition in the gas phase, as described by equation (5). The SiCl$_2$ finally produces (SiCl$_2$)$_n$, as denoted by equation (6), in the gas phase and at the solid surface. The QCM sensor is expected to detect the deposition of (SiCl$_2$)$_n$ on its surface by means of measuring the significantly small weight increase at the ng/cm^2 level.

$$\text{*SiCl}_2 \;\rightarrow\; \text{SiCl}_2\uparrow \tag{4}$$

$$\text{SiHCl}_3 \;\rightarrow\; \text{SiCl}_2 + \text{HCl} \tag{5}$$

$$n\text{SiCl}_2 \;\rightarrow\; (\text{SiCl}_2)_n \tag{6}$$

The voltage applied to the halogen lamps was fixed at 80 V. Because the trichlorosilane gas absorbs a part of the infrared light emitted from the halogen lamps [9, 21], the gas phase temperature, and consequently the wafer temperature, increased with the increasing trichlorosilane gas concentration. For monitoring the thermal condition, the temperature at the top of the wafer rotation shaft, T_{Shaft} ($^{\circ}$C), shown in Fig. 1, was measured using the R-type thermocouple. The T_{Shaft} value was considerably different from the wafer surface temperature, T_{Surface}, shown in Fig. 1 due to the distance between them [9].

The QCM sensor (25 MHz, Hallolan Electronics Co., Ltd., Tokyo) was installed at the exhaust, as shown in Fig. 1, for avoiding the metallic contaminations due to the QCM sensor consisting of various metals. The exhaust gas entered into the QCM box, then passed over the QCM sensor surface. The QCM frequency was obtained by the controller and was recorded by a personal computer. The QCM is expected to obtain the significantly weak information [14-16] related to the silicon epitaxial growth process such as the gas property change and the byproduct deposition. Although the measurement at the exhaust might contain the results by various processes in the reactor, the major trend was expected to be obtained even from the scattering data.

Figure 2 shows the process used in this study for clearly observing the QCM frequency behavior by separating it from the temperature influence. During Steps A-B, the wafer was heated to a high temperature for cleaning the silicon wafer surface. During Steps B-C, the temperature was decreased so that the trichlorosilane did not cause any chemical reaction. During Steps C-E, the trichlorosilane gas was introduced into the reactor. By this sequence, the trichlorosilane introduction could be clearly detected by the QCM frequency shift. During Steps D-E, the wafer temperature was increased by means of increasing the halogen lamp voltage in order to initiate the silicon epitaxial growth. Two minutes after increasing the halogen lamp voltage, the epitaxial growth was automatically initiated by the high temperatures. After maintaining Step D for an additional one minute in order to produce the silicon epitaxial film, the wafer was cooled at Step E. At the same time, the trichlorosilane gas supply was terminated. After taking out the wafer from

the reactor, the epitaxial film thickness was evaluated by measuring the increase in the wafer weight and the wafer thickness.

Because the exhaust pipe (1/4-inch diameter) between the quartz tube and the QCM box was sufficiently long and thin, about a 0.5-m length and 0.25-inch diameter, respectively, the exhaust gas was sufficiently cooled to room temperature. Thus, any temperature change around the wafer did not influence the QCM frequency.

As reported in a previous study [13], the QCM frequency change is proportional to the product of the gas density, ρ, and gas viscosity, μ, to the 1.3-th power, $(\rho \mu)^{1.3}$. As shown in Fig. 3, the $(\rho \mu)^{1.3}$ value is nearly proportional to the mole fraction of the trichlorosilane gas in ambient hydrogen at room temperature and at atmospheric pressure. Based on Fig. 3, the QCM frequency change corresponds to the increase and decrease in the trichlorosilane gas concentration.

3. Results and discussion

3.1 Temperature and film thickness

The relationships between the T_{Shaft} value, the $T_{Surface}$ value and the obtained film thickness were evaluated. Figure 4 shows the silicon epitaxial film thickness obtained for one minute at various temperatures in this study. The film thickness increased with the increasing T_{Shaft} value following the Arrhenius plot. There was a simple relationship between the T_{Shaft} value and the film thickness. At a temperature higher than 470-480 °C, the film thickness became nearly 1 μm.

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The wafer surface temperature, $T_{Surface}$, was evaluated using the silicon epitaxial growth rate. When the epitaxial film is formed at temperatures lower than 1000 ℃ and at trichlorosilane gas concentrations higher than about 1%, the silicon epitaxial growth rate is determined by the rate of equation (2). Because the hydrogen concentration is nearly constant at atmospheric pressure, the epitaxial growth rate is described as a function of the wafer surface temperature, $T_{Surface}$, [9, 21] as follows:

$$\text{Growth rate (μm/min)} = 1.95 \times 10^9 \, e^{(-26100/T_{Surface})} \quad (T_{Surface}<1000℃). \tag{7}$$

Figure 5 shows the $T_{Surface}$ values obtained by equation (7) that determinines the film thickness in Fig. 4. In this figure, the T_{Shaft} value showed a simple relationship with the $T_{Surface}$, while the difference between these values was as high as 400 – 500 ℃. This relationship was valuable for the various evaluations in this study, because the T_{Shaft} value is the only real time measurable temperature in this reactor.

3.2 QCM frequency behavior along with the epitaxial growth process

Figure 6 shows the typical QCM frequency behavior corresponding to the various operations along with the silicon epitaxial growth processes. In this figure, the F (Hz) is the difference from the intrinsic frequency (25 MHz).

In this figure, A, B, C, D and E indicate the same operations as those shown in Fig. 2. ΔF is the QCM frequency shift caused by the trichlorosilane gas introduction. dF/dt denotes the QCM frequency gradient during the silicon epitaxial growth. D' indicates the time at which the QCM frequency gradient slightly changed.

One of the characteristic behaviors is the QCM frequency from Steps A to C. During Steps A-B, the wafer temperature was increased from room temperature to the high temperatures in order to remove the native oxide film at the silicon wafer surface in ambient hydrogen. Additionally, the wafer was cooled again during Steps B-C to a moderately high temperature. Although the QCM frequency is quite sensitive to the temperature, the QCM frequency was not influenced even by such a significant temperature change. This indicated that the exhaust gas could be sufficiently cooled to room temperature before reaching the QCM box by means of the flowing air around the exhaust tube. This result indicated that the distance between the quartz tube and the QCM box could be reduced in order to make the response time shorter.

In contrast, immediately after introducing the trichlorosilane gas at Step C, the QCM frequency quickly decreased about 1000 Hz. Because this change occurred before increasing the wafer temperature at Step D, the QCM frequency shift after Step C was due to the gas property change following the relationship shown in Fig. 3. Immediately before Step D, the trichlorosilane concentration in the reactor approached a steady state. After the Step D heating of the wafer surface to a high temperature for initiating the silicon epitaxial growth, the QCM frequency gradient

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slightly increased at Step D'. Taking into account the time necessary for heating and for reaching the gases from the hot wafer to the QCM box, this frequency gradient change could be the initiation of the byproduct, $(SiCl_2)_n$, production in the reactor and deposition at the QCM sensor surface. This assumption was reasonable because the QCM frequency became flat soon after terminating the heating and the trichlorosilane supply at Step E. Along with purging with hydrogen gas, that is, the decreasing $(\rho\mu)^{1.3}$, the QCM frequency again increased to a higher value and lower than the initial frequency. The difference in the QCM frequency between that at Step A and that a long time after Step E might correspond to the deposition on the QCM sensor surface.

3.3 ΔF

Figure 7 shows the relationship between the ΔF value and the T_{Shaft} value during the epitaxial growth. As described in the Experimental section, the trichlorosilane gas absorbs a part of the infrared light [9, 21] to increase the gas phase temperature in the reactor. This behavior could help to increase the wafer temperature. At the trichlorosilane concentration of 0 %, that is, at the ΔF value of 0 Hz, the T_{Shaft} value was near 400 ^{o}C. With the increasing ΔF value from 0 to 1500 Hz, the T_{Shaft} value increased to about 500 ^{o}C.

The T_{Shaft} value increases with the increase in the $T_{Surface}$ value causing an increase in the silicon epitaxial growth rate. Figure 8 shows the relationship between the obtained film thickness and the ΔF value. While there was a considerable fluctuation, this figure shows the trend in the

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film thickness increase with the increasing ΔF value. This indicated the possibility for predicting the obtained film thickness immediately after Step C.

During the silicon epitaxial growth, the QCM frequency was assumed to decrease corresponding to the byproduct deposition on the QCM sensor surface. Assuming that the thermal and chemical conditions governed the production of both the silicon epitaxial film and the byproduct, $SiCl_2$, the dF/dt value given by the byproduct production should have a relationship with the silicon epitaxial film formation.

3.4 dF/dt

Figure 9 shows the behavior of the dF/dt value with the increasing T_{Shaft} value. When the T_{Shaft} value was lower than 450 ^{o}C, corresponding to the film thickness less than about 0.5 μm, the dF/dt value was nearly zero Hz/s. Due to the very low temperature, the byproduct production was not detectable. At the T_{Shaft} value higher than 450 ^{o}C, the dF/dt value became significant. At the T_{Shaft} value of 490 ^{o}C, the dF/dt value was about -4 Hz/s.

Because the $T_{Surface}$ value increased with the increasing T_{Shaft} value, the obtained film thickness should show a relationship with the dF/dt value. This prediction was verified in Fig. 10. In the obtained film thickness region of less than 0.5 μm, the dF/dt value was almost 0 Hz/s. However, with the increasing film thickness, the dF/dt value average in the region had negative values, not positive values. Overall, the dF/dt value is concluded to have a relationship with the

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obtained film thickness.

Because the ΔF and dF/dt values corresponded to the trichlorosilane concentration and the obtained film thickness, respectively, there should be a relationship between them. Figure 11 shows the simple linear relationship between the ΔF and dF/dt values. This practically indicated that the high growth rate could be predicted at the early step of the silicon epitaxial growth based on the ΔF behavior immediately after the trichlorosilane gas introduction.

3.5 Thermal and chemical conditions

Taking into account the various information obtained in this study, the behaviors of the ΔF value and the dF/dt value are summarized in Figs. 12 and 13. The radiation heat of the infrared light is absorbed not only by the silicon wafer surface, but also by the trichlorosilane gas in the gas phase, as shown in Fig. 12. The effective heat absorption increases the $T_{Surface}$ value. Particularly, the $T_{Surface}$ value increases with the increasing trichlorosilane concentration, which is measured as the ΔF value by the QCM. Additionally, the $T_{Surface}$ value increases the T_{Shaft} value by the heat conduction through the three silicon carbide plates and the quartz plate.

The thermal condition shown in Fig. 12 induces various chemical reactions, as shown in Fig. 13. The trichlorosilane that reached the hot silicon surface produces the silicon epitaxial film. Simultaneously, a significantly small amount of $SiCl_2$ is produced as the byproduct in two ways,

such as *i)* in the gas phase by the thermal decomposition and *ii)* from the surface by the $*SiCl_2$ desorption. Because of the cold wall environment in the reactor, the high temperature region possible for the trichlorosilane thermal decomposition is limited to that near the hot wafer surface. A part of the $SiCl_2$ finally produces the $(SiCl_2)_n$ deposition at the QCM sensor surface thus causing the negative dF/dt value.

In summary, the side reactions of the $SiCl_2$ production by both *i)* and *ii)* are mainly governed by the $T_{Surface}$ value. The high trichlorosilane gas concentration, measured as the ΔF, produces the high values of $T_{Surface}$ and T_{Shaft}. The high $T_{Surface}$ value produces the high epitaxial growth rate while slightly producing the $(SiCl_2)_n$, measured as the dF/dt. Thus, taking into account the ΔF value measured by the QCM during the early stage, the obtained film thickness is expected to be predicted and finely adjusted.

3.6 QCM frequency for trichlorosilane gas operation

The practical problem and operation are explained by taking into account the situation in the trichlorosilane bubbler. Because the vapor pressure of the liquid trichlorosilane at room temperature [19] is low, any additional vaporization technique is useful for supplying a sufficient amount of trichlorosilane gas to the epitaxial reactor. The hydrogen gas is usually injected into the liquid trichlorosilane for producing small gas bubbles containing the trichlorosilane vapor. By such a simple operation, the gas mixture of trichlorosilane and hydrogen is produced and supplied at

the trichlorosilane concentration corresponding to the temperature of the liquid trichlorosilane.

For increasing the trichlorosilane gas concentration, the liquid container is often heated to temperatures slightly higher than room temperature. The heating operation easily and effectively increases the vapor pressure to increase the trichlorosilane concentration. However, because the vapor pressure depends on the temperatures near the boiling point, 31 $^{\circ}$C, the trichlorosilane concentration in the gas mixture often fluctuates. In such a situation, the *in-situ* on-time measurement of the trichlorosilane concentration by the ΔF value is expected to be used for adjusting the trichlorosilane gas concentration in order to reproduce the epitaxial growth condition. For example, when the ΔF value is low and high, the halogen lamp voltage can be finely adjusted to high and low, respectively. Additionally, by the *in-situ* real time evaluation of the the formed film thickness by the dF/dt value, the time period for the epitaxial film formation is expected to be adjusted.

In addition, various applications are expected. The data obtained by the QCM have considerable fluctuation, as shown in Figs. 4, 5 and 7-11. The information obtained at the outlet, such as that by the QCM in this study, tends to contain those from whole processes happened in the reactor. In other words, any adjusting and tuning for reducing the fluctuation in the various process conditions will be evaluated by the reduction of the QCM data fluctuation at the exhaust. The control technique of various parameters will be developed, improved and verified by monitoring the QCM frequency behaviour. Particularly, such the study will improve the

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reproducibility of any temperatures relating to any chemical reactions at the substrate, at the wafer holder, at the quartz tube surface, at the reflector surface at the halogen lamps and in the gas phase.

4. Conclusions

An *in-situ* real time evaluation of the silicon epitaxial growth process in a trichlorosilane-hydrogen system was studied using the simple classical system of a quartz crystal microbalance (QCM). The QCM placed at the exhaust of an epitaxial reactor for the Minimal Fab showed characteristic behaviors which could be classified to two types. The first was a quick shift due to the gas property change caused by the trichlorosilane gas introduction into the ambient hydrogen. This can monitor the trichlorosilane concentration that actually arrives at the reactor. The second was the continuous gradual decrease due to the byproduct deposition on the QCM surface. This has a correlation with the chemical reaction rate for producing the silicon epitaxial film and the $SiCl_2$ byproduct in the reactor. The *in-situ* real time information obtained by the QCM was expected to monitor and control the film deposition process, such as those for stabilizing the trichlorosilane gas concentration and for adjusting the film thickness.

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Figure captions

Figure 1   Chemical vapor deposition reactor for Minimal Fab., having a quartz crystal microbalance.

Figure 2 Silicon epitaxial growth process used in this study. A: heater on, B: temperature decrease, C: initiate trichlorosilane supply, D: temperature increase and E: terminate trichlorosilane supply and heater off.

Figure 3 Relationship between mol fraction of $SiHCl_3$ and $(\rho\mu)^{1.3}$ at room temperature and atmospheric pressure.

Figure 4 Silicon epitaxial film thickness changing with the temperature at rotation shaft top, T_{Shaft}.

Figure 5 Relationship between temperature at rotation shaft top, T_{Shaft} and substrate surface temperature, $T_{Surface}$.

Figure 6 QCM frequency, F (Hz), measured along with the silicon epitaxial growth process. A, B, C, D and E correspond to the same letters in Fig. 2. ΔF: QCM frequency shift by trichlorosilane introduction after Step C. dF/dt: QCM frequency gradient between Steps D and E. D' is the time at which dF/dt slightly changed.

Figure 7 Relationship between QCM frequency shift by trichlorosilane introduction, ΔF, and temperature at rotation shaft top, T_{Shaft}.

Figure 8 Relationship between QCM frequency shift by trichlorosilane introduction, ΔF, and obtained film thickness.

Figure 9 Relationship between temperature at rotation shaft top, T_{Shaft} and QCM frequency gradient, dF/dt.

Figure 10 Relationship between film thickness and QCM frequency gradient, dF/dt.

Figure 11 Relationship between QCM frequency shift by trichlorosilane introduction, ΔF, and QCM frequency gradient, dF/dt.

Figure 12 Thermal condition and chemical processes in Minimal silicon epitaxial growth process.

Figure 13 Production of Si film, $SiCl_2$ and $(SiCl_2)_n$.

H$_2$

SiHCl$_3$

Inlet

Lamp

Lamp

Computer

Controller

T_{Surface}

T_{Shaft}

Wafer

Quartz tube

QCM

Exhaust

QCM Box

Reactor

Thermocouple
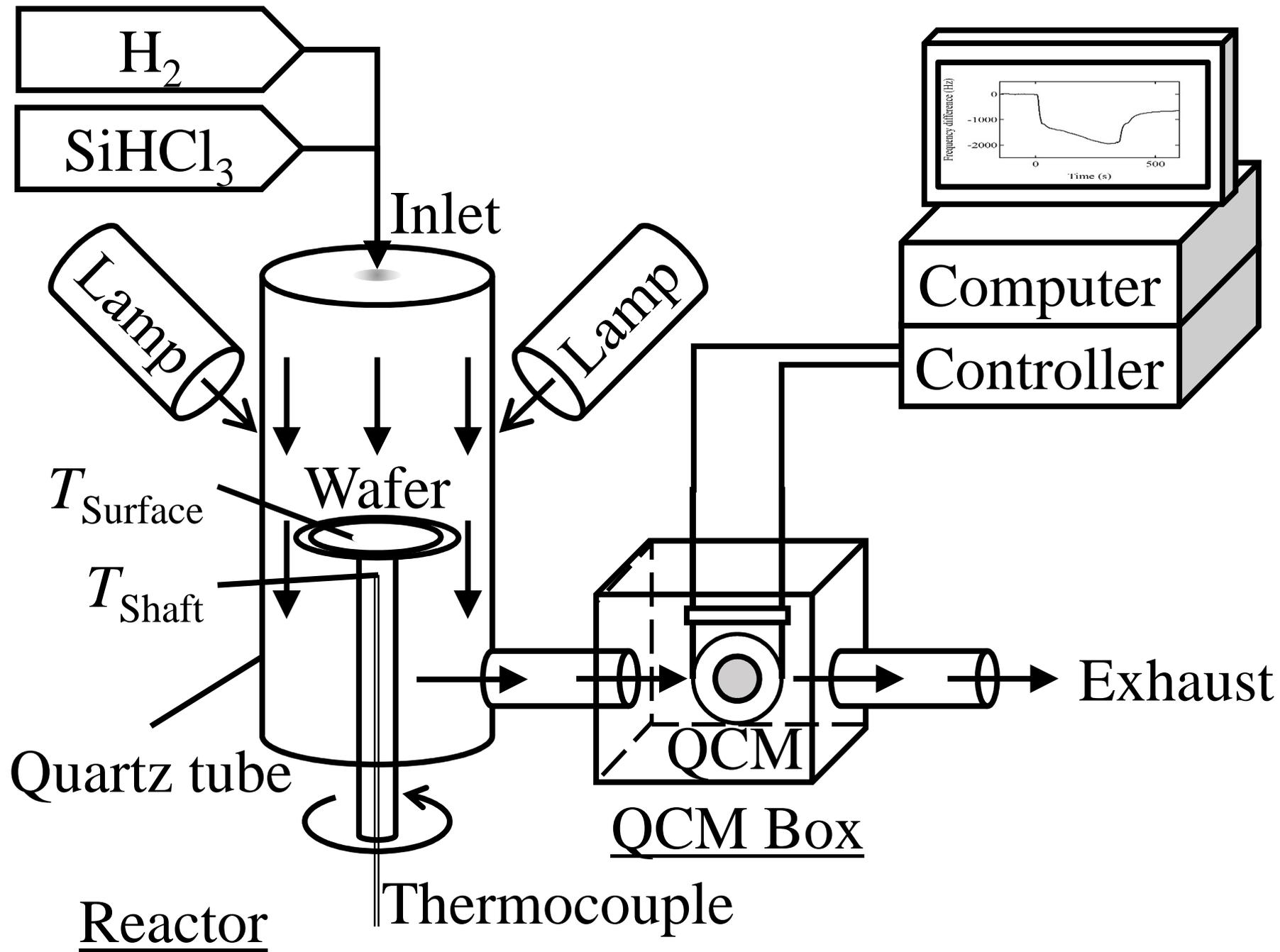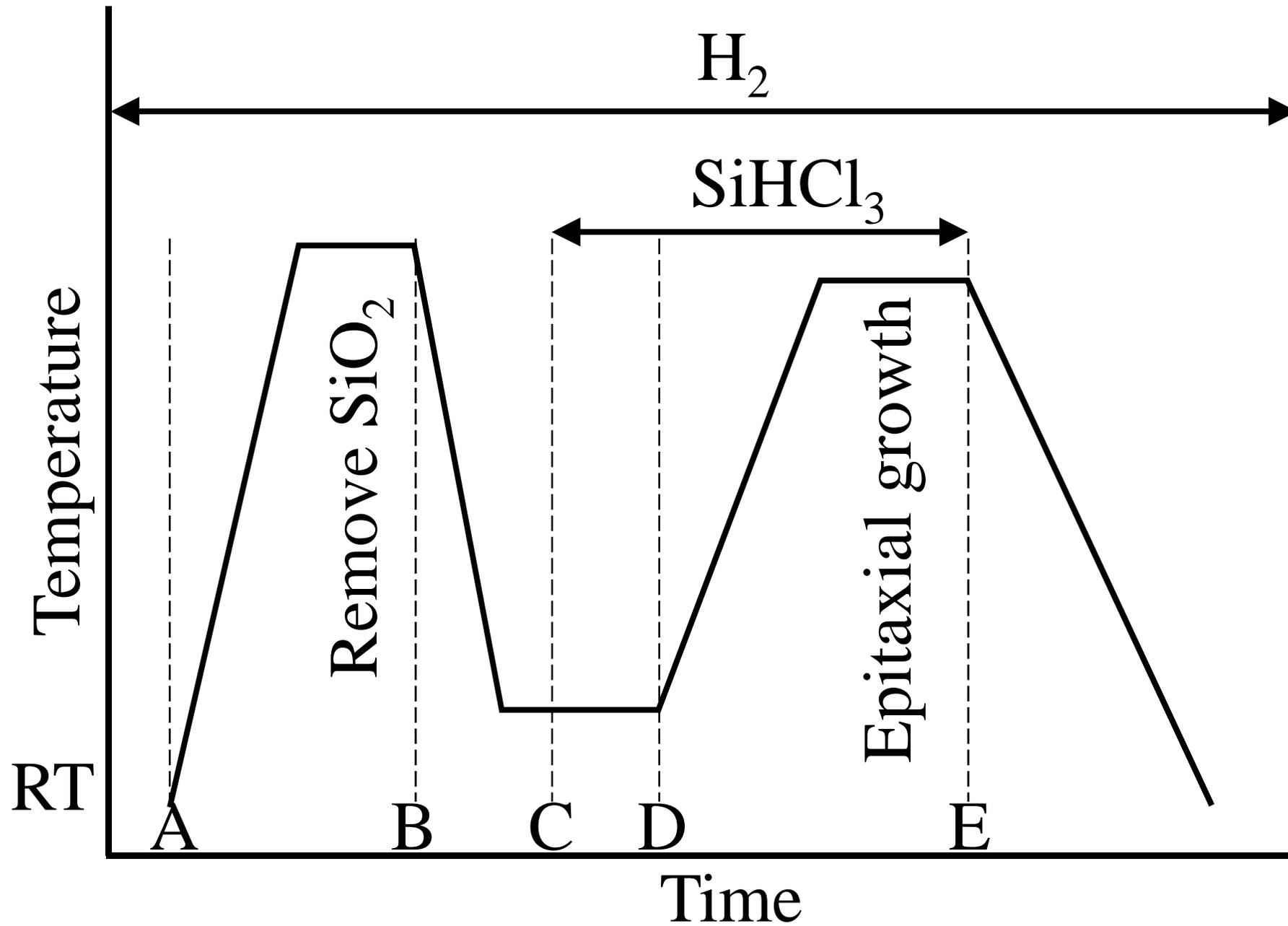
Fig. 1

Fig. 2
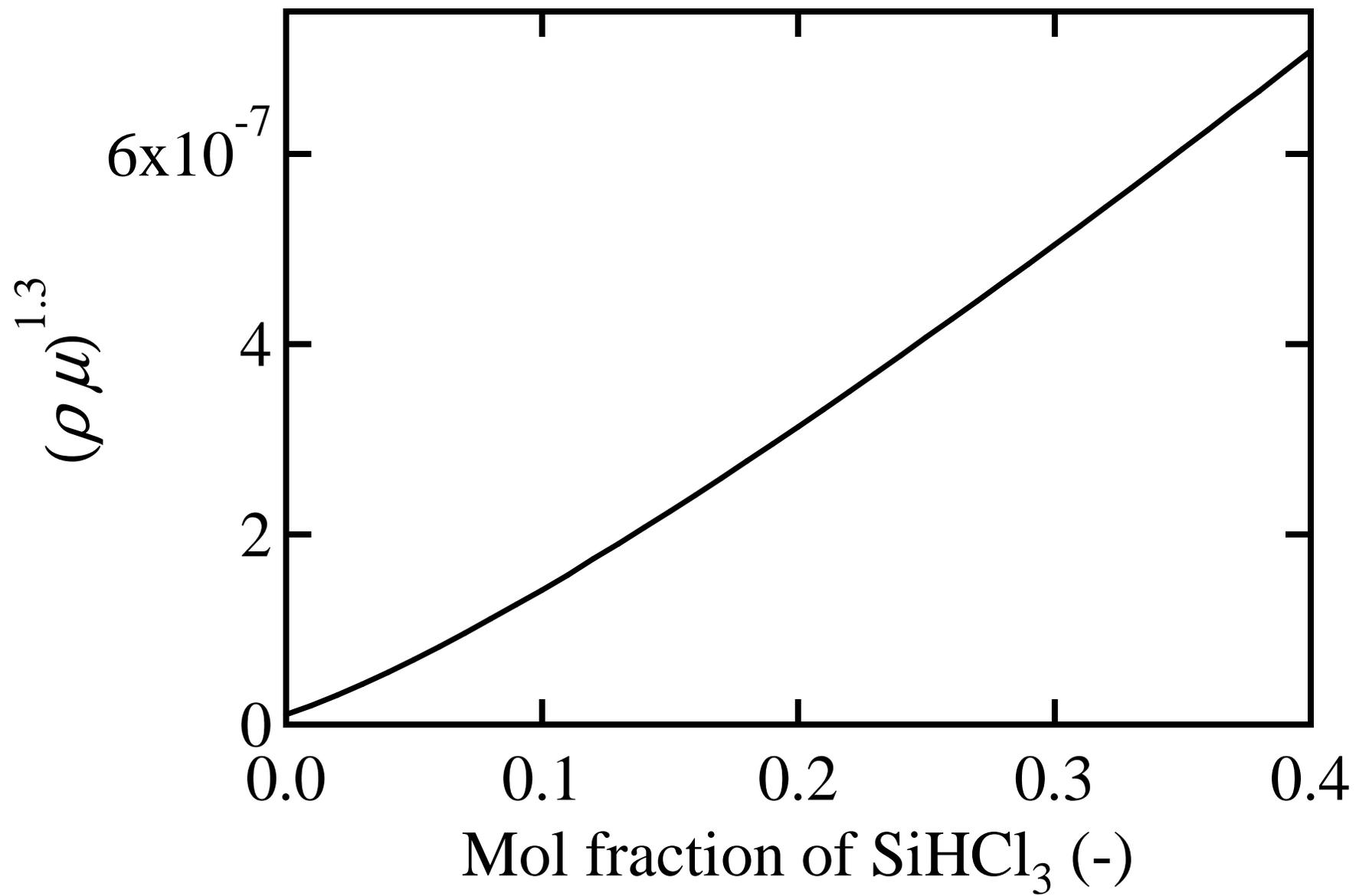
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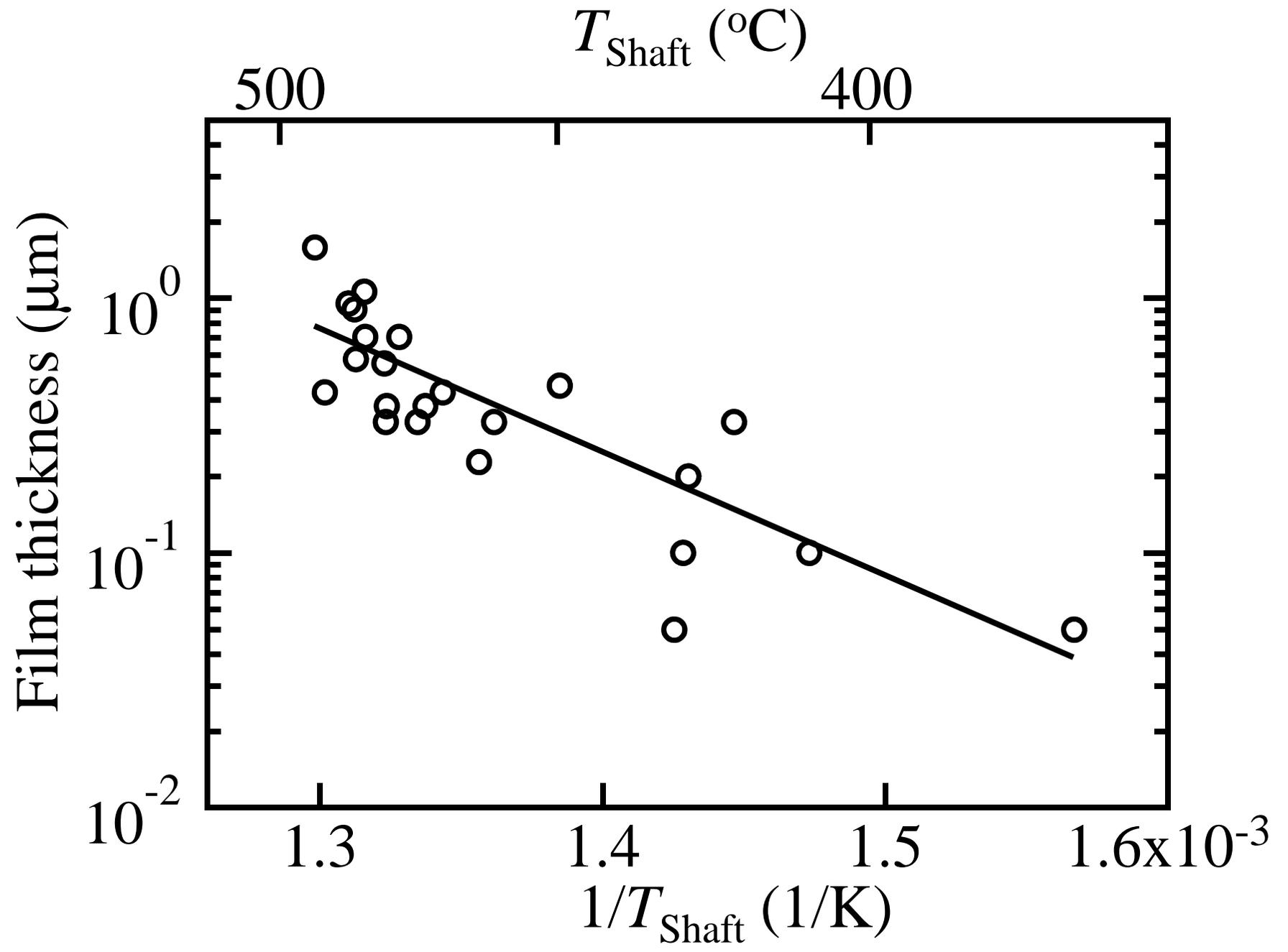
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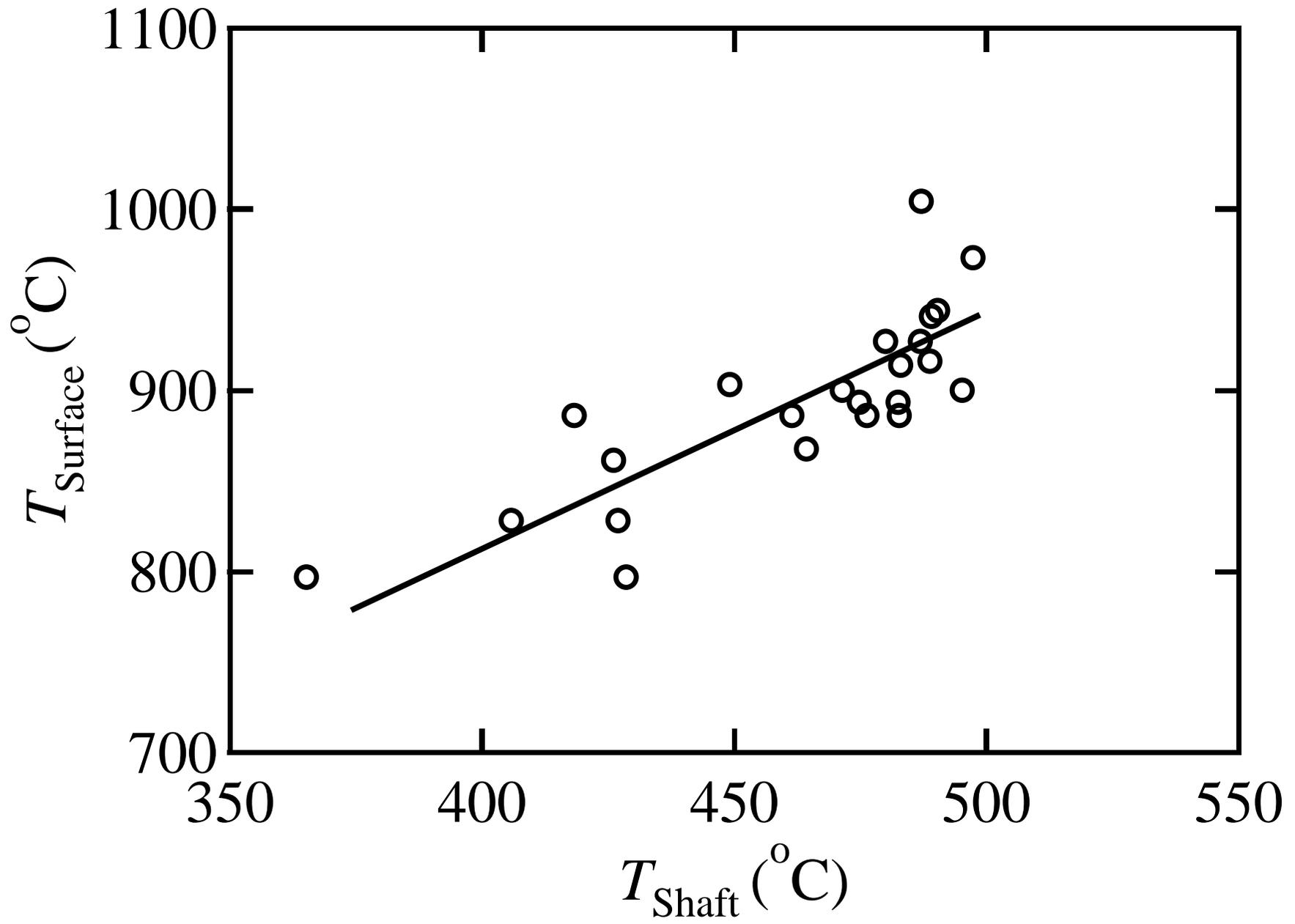
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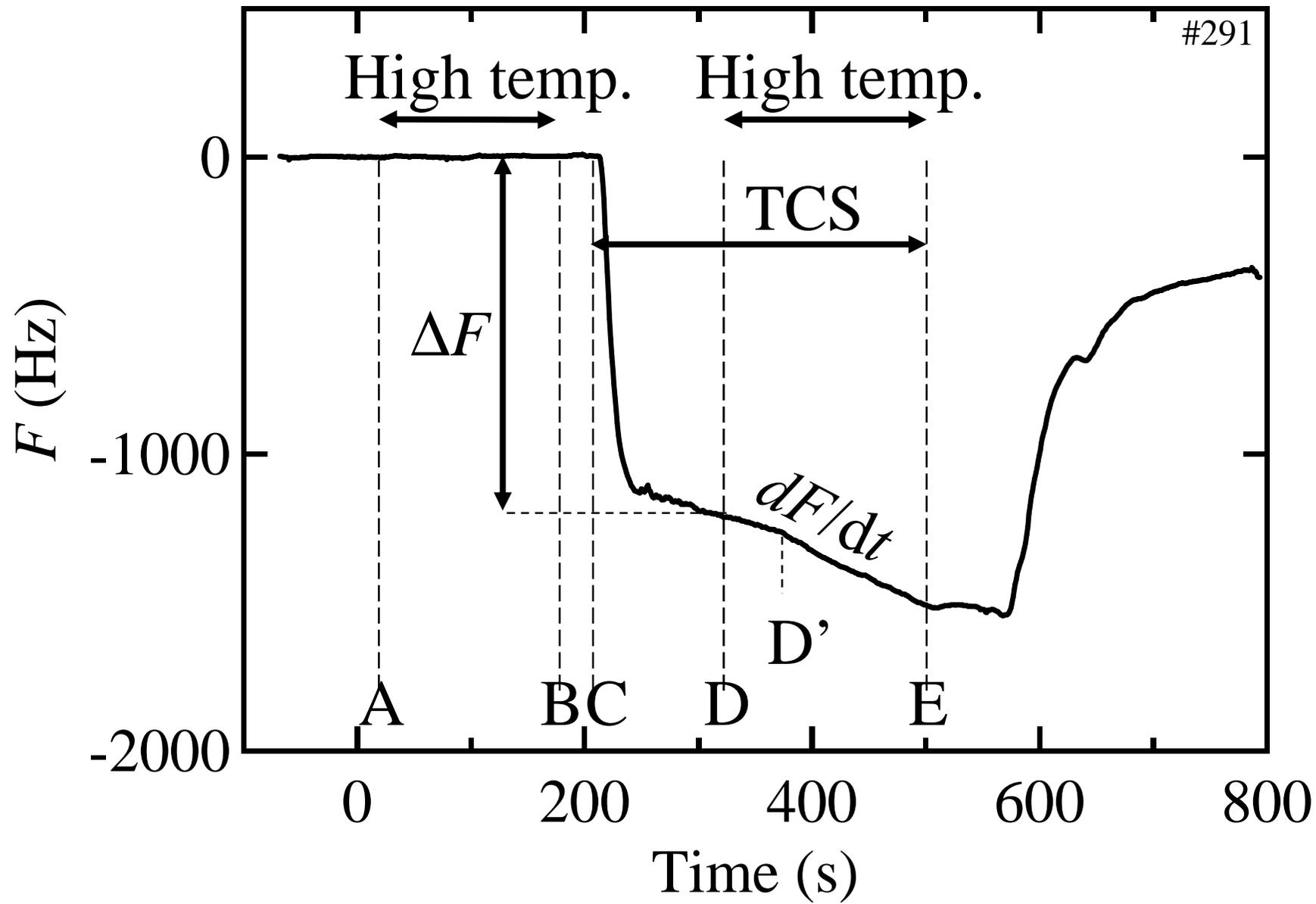
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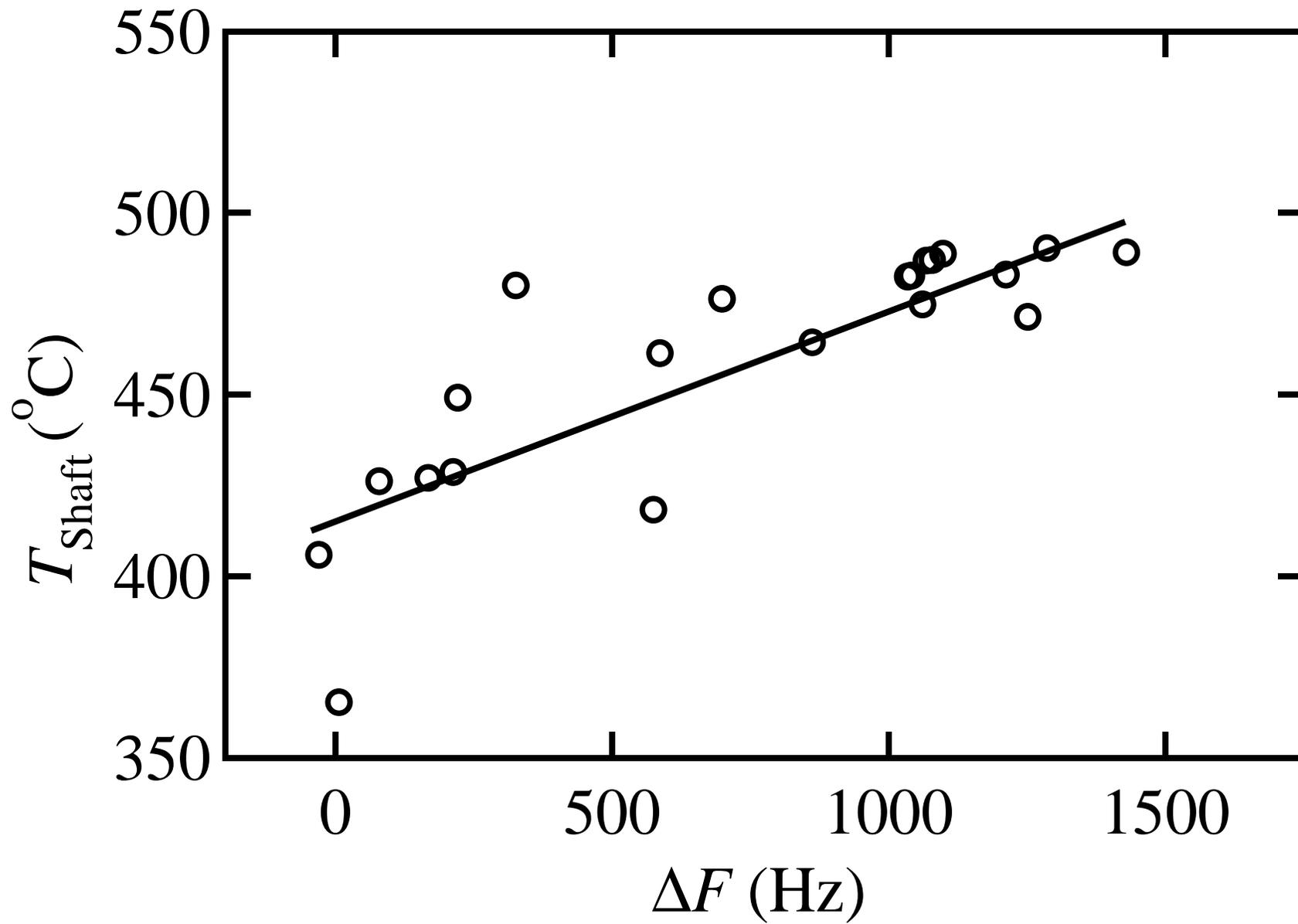
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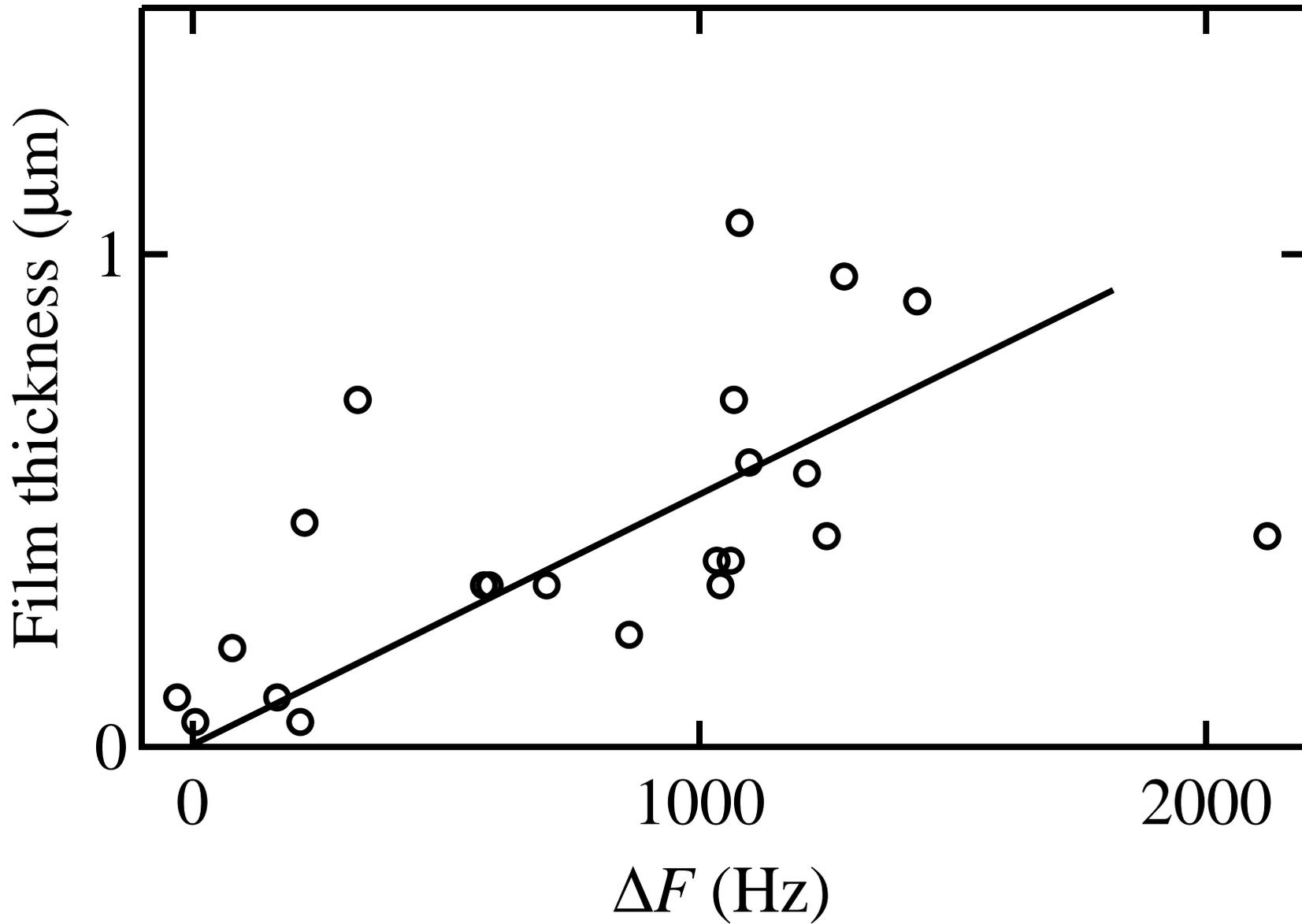
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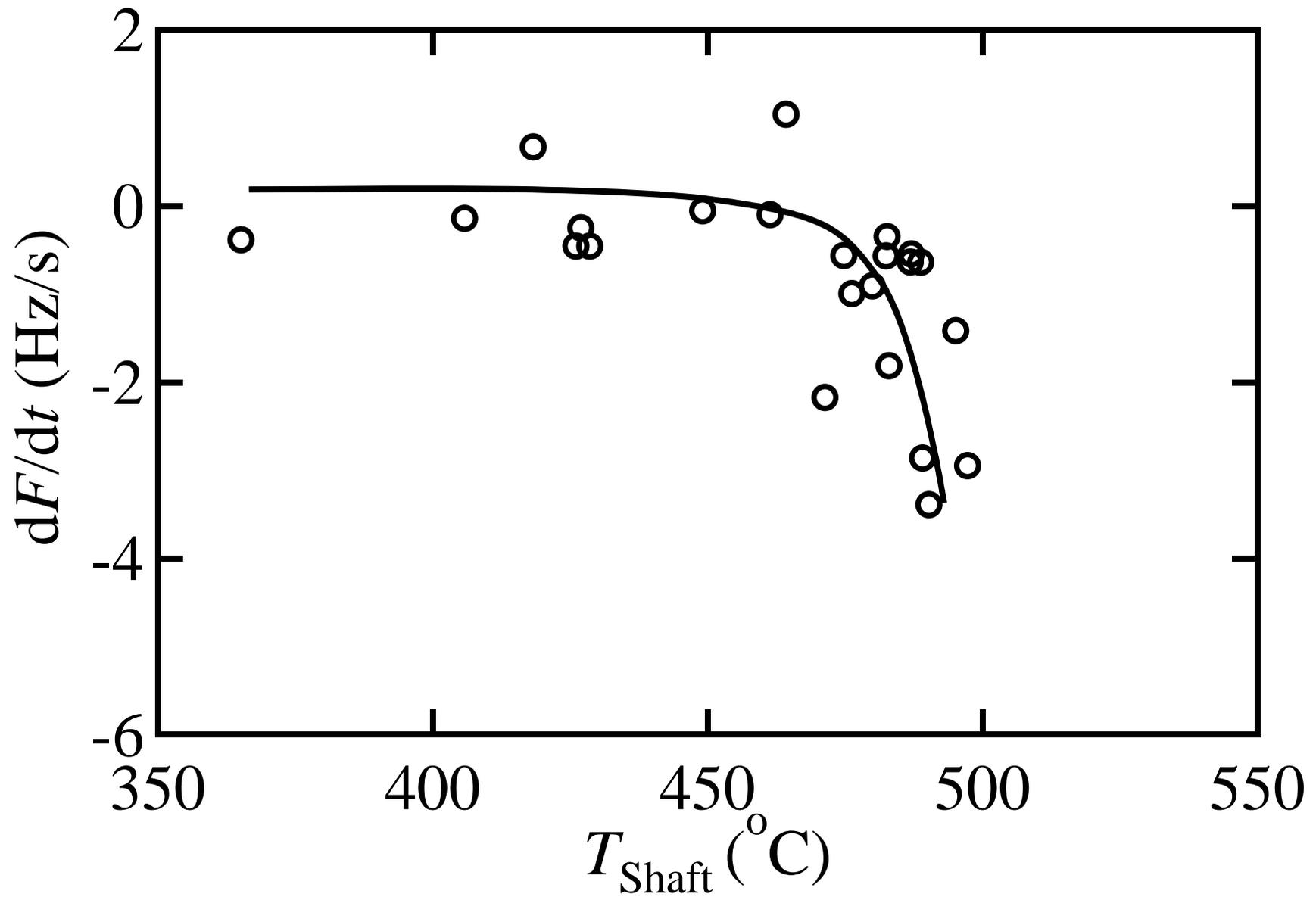
Fig. 9

Fig.10

Fig.11

Fig.12

Fig.13