In Situ Measurement for Evaluating Temperature Change Related to Silicon Film Formation in a SiHCl₃-H₂ System

Kento Miyazaki, Ayumi Saito, and Hitoshi Habuka*²

Department of Chemical and Energy Engineering, Yokohama National University, Hodogaya, Yokohama, Kanagawa 240-8501, Japan

The temperature change related to silicon film formation in a trichlorosilane-hydrogen system was evaluated by an in situ monitoring method using the langasite crystal microbalance (LCM). First, the time constants for the LCM frequency change due to the surface and gas phase temperature change were determined to be less than two hundred seconds. The continuous LCM frequency decrease appearing two hundred seconds after changing the trichlorosilane gas concentration was assigned to the weight increase by the film formation in a steady state. Based on an evaluation of the difference in the LCM frequency between those with and without the heat change related to the film formation, the surface temperature decrease caused by slightly changing the trichlorosilane concentration was comparable to one degree.

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Chemical vapor deposition (CVD) is one of the most popular techniques for producing a high quality film for manufacturing various advanced devices, such as the ultra-large scale integrated circuits (ULSI) and microelectromechanical systems (MEMS). It can produce very uniform films from very thin to thick, such as nanometers to hundred microns, by finely controlling various parameters, such as the pressure, gas flow rates, precursor gas concentrations and temperatures in the gas phase and at the substrate surface. The temperature of the surface for the film formation is one of the most important and difficult parameters to be evaluated and controlled. The surface temperature is affected not only by the heat transport via the gas phase from the heating devices, but also by the heat change in situ produced due to the precursor.

In order to reveal and clarify the temperature behavior related to the film formation, an in situ monitor, such as the langasite crystal microbalance (LCM), has been expected to be used. It can work at the high temperatures required for film formation. Additionally, the LCM can sensitively respond to various parameters, such as the temperature, the gas density and the gas viscosity.2–6

In order to develop the in situ monitoring technique applicable for the CVD process, our previous studies showed that the LCM frequency could be a function of the product of the gas density and the gas viscosity in the CVD reactor. Additionally, the lowest temperature region for the silicon and silicon carbide film formation was evaluated.

In addition to these studies performed in a steady state, the CVD process in a non-steady state, such as that immediately after initiating the film formation by introducing the precursor gases, should be clarified. The addition of the precursors changes the heat capacity, the heat conduction and the reaction heat in the reactor that affect the film formation by introducing the precursor gases, should be "clarified."

The typical process used in this study is shown in Fig. 2a. First, the LCM was heated to 380–660 °C in ambient hydrogen at atmospheric pressure. With the increasing temperature, the LCM frequency decreased. After waiting until the LCM frequency became stable, the trichlorosilane gas was introduced at atmospheric pressure into the reactor chamber. The total flow rate of the hydrogen gas and trichlorosilane gas was 1.0 slm at atmospheric pressure. The concentration of hydrogen gas and trichlorosilane gas was 99.4–97.0% and 0.06–3.0%, respectively. The trichlorosilane gas concentration was stepwise increased, as shown in Fig. 2b.

**Experimental**

**Reactor and process.**— Figure 1 shows the horizontal cold wall reactor in which the LCM was installed at the center position. This reactor consisted of a gas supply system, a quartz chamber and infrared lamps. The gas supply system can introduce hydrogen, nitrogen and trichlorosilane gases. Hydrogen is the carrier gas. The gas flow channel of this reactor has a low height and a small rectangular cross section in order to achieve a high consumption efficiency of the reactive gases. The height and width of the quartz chamber were 10 mm and 40 mm, respectively, similar to those used in our previous studies.7–12

A 30-mm-wide × 30-mm-long (100) silicon wafer manufactured by the Czochralski method was horizontally placed on the bottom wall of the quartz chamber and at a position in which the infrared flux from the halogen lamps could be effectively received. The LCM (Halloran Electronics, Tokyo, Japan) was placed 5 mm above the silicon wafer and was connected to a personal computer in order to record its frequency.

The LCM has an intrinsic frequency of 10 MHz similar to our previous studies.6–11 The silicon wafer and the LCM were simultaneously heated by infrared light from the halogen lamps through the quartz chamber. The LCM was heated not only by the infrared light, but also by radiation heat and conduction heat from the hot silicon wafer. Because the LCM and the silicon wafer were very close, the temperature of the LCM was assumed to be the same as that of the silicon wafer. The temperature of the silicon wafer was measured prior to the film deposition process using thermocouples.

The electrode of the LCM was made of iridium, because it is inert to various chemicals. Prior to measuring the film deposition, the entire LCM surface was coated with a silicon carbide film in order to suppress damage by the ambient hydrogen and for easily allowing silicon nucleation.

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**LCM frequency behavior.—** The LCM frequency decreases corresponding to the weight increase on the LCM surface, following the Sauerbrey equation:

\[
\Delta f = - \frac{A \Delta m f_0^2}{\mu_s \rho_c^{1/2}},
\]

where \(\Delta f\) is the measured resonant frequency decrease, \(f_0\) is the intrinsic crystal frequency, \(A\) is the elastic mass change, \(A\) is the
gas mixture. The modulus of the crystal. Similar to previous studies, the LCM used in this study is assumed to obey Equation 1.

Other than the temperature and the film weight, the LCM frequency changes with the fluid properties, as described by Equation 2.

where $\rho$ is the density and $\eta$ is the viscosity, respectively, of the gas mixture. The $\eta$ value is obtained from the literature. The $x$ value was evaluated to be 1.3 in our previous study. These parameters produce typical changes in the LCM frequency during the entire CVD process. The change in the LCM frequency related to the film deposition by the trichlorosilane gas could be classified by Parameters (i) – (viii) schematically shown in Fig. 3.

Parameter (i) in Fig. 3 is the pressure and concentration of the gas remaining in the gas system. The LCM frequency very quickly and slightly increased due to the pressure increase in the reactor when opening the trichlorosilane gas valve. Following this, the LCM frequency decreased and recovered for a short period corresponding to the trichlorosilane gas remaining at a high concentration between the mass flow controller and the gas valve, reaching and passing the reactor.

Parameter (ii) is the $(\rho \eta)^{1.3}$ value of the gas mixture. Corresponding to this, the LCM frequency decreases from the initial frequency.

Parameter (iii) is the weight increase due to the film deposition. After a sufficient time for reaching a steady-state, the weight increase of the film formed on the LCM can be observed as a continuous and linear decrease in the LCM frequency.

Parameter (iv) is the reaction heat. The silicon film formation is an endothermic reaction. This decreases the temperature and thus increases the LCM frequency. With the addition of the trichlorosilane gas, the film formation quickly begins and continues till termination of the trichlorosilane gas supply.

Parameter (v) is the weight increase due to the film deposition. After a sufficient time for reaching a steady-state, the weight increase of the film formed on the LCM can be observed as a continuous and linear decrease in the LCM frequency.

Parameter (vi) is the $(\rho \eta)^{1.3}$ value. The decrease in this value immediately causes the LCM frequency to shift to a high value when the trichlorosilane gas supply is terminated.

Parameter (vii) is the heat capacity and the heat conduction. Due to the heat capacity decrease because of the lack of trichlorosilane gas, the gas phase temperature gradually increases and causes a decrease in the LCM frequency.

Parameter (viii) is the weight increase due to the film deposition. After a sufficient period for achieving a steady-state, the LCM frequency shift from that before the trichlorosilane gas supply corresponds to the increased weight of the film formed on the LCM.

If the temperature change due to the trichlorosilane gas did not exist, the temperature during the early stage of the film formation behaves like the thick dotted line, as shown in Fig. 3. Thus, the LCM frequency difference between the solid line and the thick dotted line is considered to be a function of the temperature shift.

**Reaction heat and heat transport.** By introducing the trichlorosilane gas into the reactor, the silicon film formation occurs along with the endothermic reaction heat, and change of the physical properties of the gas mixture, as shown in Fig. 4. Thus, the multiple thermal processes change the temperature of the surface on which the film is formed. In this study, the influence of each parameter was evaluated, following Steps 1, 2 and 3, as shown in Fig. 5, taking into account the time constant for heat transport.

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**Figure 1.** Horizontal cold-wall chemical vapor deposition reactor. The LCM was installed in the quartz chamber.

**Figure 2.** Entire process consisted of (a) gases and temperature operation and (b) the typical change in trichlorosilane gas flow rate.

**Figure 3.** Schematic of changes in the frequency and the temperature of the LCM influenced by parameters (i) – (viii). Parameter (i): pressure and concentration of gas remaining in the gas system, Parameter (ii): $(\rho \eta)^{1.3}$, Parameter (iii): heat capacity, Parameter (iv): reaction heat, Parameter (v): weight increase due to the film deposition, Parameter (vi): $(\rho \eta)^{1.3}$, Parameter (vii): heat capacity and, Parameter (viii): weight increase due to the film deposition.
Figure 4. Three steps for evaluating temperature change during film deposition.

During Step 1, the time constant for the surface temperature shift was evaluated without introducing a precursor in the ambient hydrogen. The quick lamp power decrease was assumed to show a significantly quick surface temperature decrease similar to that by the endothermic surface chemical reaction, as shown in Fig. 4. After this, the gas phase temperature of the near-surface region gradually decreased. These two processes were expected to have different time constants, such as very short and slightly long.

During Step 2, the influence of the change in the heat capacity and the heat conduction of the gas mixture were studied. The time constant for the gas phase temperature shift induced by the precursor introduction, as shown in Fig. 4, was evaluated at sufficiently low temperatures at which no chemical reaction occurred. The time constant for this process was expected to be longer than those for Step 1, because the gas phase temperature shift occurred in the entire region of the reactor and not limited to the region near the surface.

During Step 3, the temperature change related to the film deposition was evaluated, accounting for the time constants obtained in Steps 1 and 2. During Step 3, the trichlorosilane concentration was stepwise changed from 0 to 3%. After the period corresponding to the time constants obtained in Steps 1 and 2, the LCM frequency behavior was recognized to be expressing the film formation in a steady state. By extrapolation, the LCM frequency immediately after changing the precursor concentration was obtained and used for evaluating the temperature shift related to the film formation.

Results and Discussion

Temperature and frequency.— First, the entire frequency dependence on the temperature is shown in Figure 6. This shows the frequency difference at various temperatures from that at room temperature. With the increasing temperature, the LCM frequency decreased, as shown in Fig. 6a. At the higher temperatures, the LCM frequency more rapidly decreased than that at the lower temperatures. The temperature gradient was evaluated as shown in Fig. 6b. The gradient decreased with the increasing temperature. At 450, 550 and 650°C, the LCM frequency gradient was −240, −390 and −440 Hz/K, respectively. The frequency change due to the temperature change was about −400 Hz/K in the temperature range between 500 and 650°C.

Heat at surface.— In order to evaluate the LCM frequency behavior caused by the quick surface temperature decrease, such as that by the reaction heat, the LCM frequency influenced by the stepwise lamp power shift was measured and evaluated, as shown in Figure 7. The lamp power corresponding to about 1 K quickly decreased at 450°C and 660°C.

Figures 7a and 7b show the normalized LCM frequency change caused by the stepwise lamp power shift at 450°C and 660°C, respectively. In both figures, the LCM frequency very quickly increased immediately after changing the lamp power. It then moderately increased and reached the steady state.

These behaviors were expressed assuming that the relaxation process consisted of fast and slow ones. At 450°C and 660°C, the LCM
Figure 8. LCM frequency change caused by the stepwise concentration change in the hydrogen gas and trichlorosilane gas at 380°C.

Frequency shift could be expressed as a function of time, $t$ (s).

$$
\Delta f = \left[ 230 \left( 1 - e^{-\frac{t}{8}} \right) + 90 \left( 1 - e^{-\frac{t}{34}} \right) \right] \text{ at 450°C.} \tag{3}
$$

$$
\Delta f = \left[ 370 \left( 1 - e^{-\frac{t}{5}} \right) + 80 \left( 1 - e^{-\frac{t}{47}} \right) \right] \text{ at 660°C.} \tag{4}
$$

In Fig. 7, Equations 3 and 4 are indicated by the dotted lines. This figure shows that the calculation could reproduce the measurement. The quick temperature change, the first term, is considered to directly follow the lamp power decrease, that is, the decrease in heat at the LCM surface. The slow temperature change, the second term, is considered to be due to the conduction heat transport between the surface and the gas phase very near the surface. The influence of the reaction heat and heat conduction on the LCM frequency is expected to appear within 10 seconds and within 50 seconds, respectively, after introducing the trichlorosilane gas.

Heat transport around surface in gas phase.— The LCM frequency changes due to the thermal properties, such as the heat capacity and the heat conductivity, were evaluated at the low temperatures so that the LCM could not undergo film deposition. Figure 8 shows that the LCM frequency change was due to the stepwise concentration change of hydrogen gas and trichlorosilane gas at 380°C. At Conditions C_c - C_e, the hydrogen concentration and the trichlorosilane concentration decreased and increased, respectively.

At the beginning of Condition C_c, the LCM frequency quickly dropped to less than $-3000$ Hz and recovered to $-1000$ Hz. The LCM frequency shift from 0 Hz to $-1000$ Hz corresponded to the increase in the gas density and the gas viscosity. Next, it gradually recovered to near $-400$ Hz. Till 500 seconds, the LCM frequency reached the steady state. The gradual recovery of the LCM frequency was considered to be a result of the temperature decrease mainly due to the increase in the heat capacity of the gas mixture. Additionally, the temperature decrease at the surface was moderated by the heat balance with the gas phase via the heat conduction.

These heat transports overlapped and appear as the gradual recovery of the LCM frequency. The LCM frequency at 380°C and at Condition C_w was expressed, as shown in Fig. 9, using the following equation.

$$
\Delta f = 164 \left( 1 - e^{-\frac{t}{120}} \right). \tag{5}
$$

From the temperature shift width shown in Fig. 6, the temperature decrease by the trichlorosilane gas concentration change at 380°C was evaluated to be about 1 K. The time constant of these process was about 120 s. The time constant in Equation 5 was longer than that of the second term in Equations 3 and 4. The time constant was assumed in this study to have a similar value at the higher temperatures, such as 600–700°C.

Film formation.— The silicon film formation was performed at 640°C along with measuring the LCM frequency, as shown in Figs. 10 and 11. The hydrogen gas concentration decreased from 100 to 97%, while the trichlorosilane gas concentration increased from 0 to 3%. Because the silicon film growth rate was saturated at this temperature, the reaction heat remained the same for Conditions C_a – C_d. Figure 10 shows that the LCM frequency change caused by the stepwise change in the concentrations of hydrogen and trichlorosilane.
At Condition C, the trichlorosilane gas was added to the hydrogen gas. The LCM frequency showed a significant drop and a quick recovery within several seconds. After the quick recovery, the LCM frequency gradually increased. After the peak appearance, the LCM frequency gradually decreased accompanying the fluctuation due to a temperature fluctuation. Conditions C, C₄, and C₆ showed a similar LCM frequency behavior without a significant drop, unlike that at the beginning of Condition C₄.

Taking into account the time constant corresponding to the various heat processes, the LCM frequency behavior was evaluated, as shown in Fig. 11. This shows the LCM behavior at Condition C₄, as an example. Immediately after increasing the trichlorosilane concentration from 1.8 to 2.4%, the LCM frequency quickly decreased to about -550 Hz due to the increase in the gas density and the gas viscosity. Next, it showed a broad bottom for about 20 seconds. The LCM frequency gradually increased from 50 seconds to 180 seconds. After showing a peak, the LCM frequency began to decrease. This decrease was considered to be due to the film formation during the steady state.

Next, the LCM frequency gradient was evaluated. The maximum and minimum values were evaluated to be 1.6 Hz/s between Points A and B and 0.77 Hz/s between Points A and C, respectively. By this operation, the LCM frequency immediately after changing the trichlorosilane concentration might be 245 to 410 Hz, as shown in Fig. 11.

In addition, the flat bottom of the LCM frequency to 20 seconds after changing the trichlorosilane concentration might be caused by the balance among the changes in the gas density, the gas viscosity, the heat capacity and the heat conductivity. In order to obtain the possible minimum frequency value, the increasing trend in the LCM frequency between 20 seconds and 180 seconds was extrapolated to that near several seconds. By this estimation, the frequency of about 50 Hz might be lower than that at the bottom.

By adding these values, the LCM frequency change due the temperature change by changing the trichlorosilane concentration from 1.8 to 2.4% was between 295 and 460 Hz. The surface temperature shift of about one degree was considered to be caused by changing the precursor concentration.

Our future study will evaluate the influence of the reaction heat by avoiding the significant drop in the LCM frequency caused by the trichlorosilane gas introduction. Additionally, the LCM should be applied to various phenomena and processes, not only the CVD.

The surface temperature change significantly influences the entire substrate temperature when the substrate is very thin. The substrate for the CVD process usually has a thickness greater than 300 μm, which is about ten times or higher than that of the LCM. Thus, the actual influence on the temperature shift of the thick substrate seems to be low. However, for controlling the very thin film formation, the temperature change evaluated in this study may have some influence.

Conclusions

The temperature behavior related to silicon film formation in a trichlorosilane-hydrogen system was evaluated by an in situ monitoring method using the langasite crystal microbalance (LCM). For this purpose, this study was done in three steps.

Step 1: The time constant for the surface temperature shift was evaluated without introducing a precursor in ambient hydrogen.
Step 2: The time constant by the change in the heat capacity and the heat conduction of the gas mixture was evaluated.
Step 3: The temperature change related to the film deposition was evaluated using the difference between the LCM frequencies with and without the heat change related to the film formation, while accounting for the temperature constants obtained in Steps 1 and 2.

The surface temperature decrease caused by slightly changing the trichlorosilane concentration was comparable to one degree.

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