The process of by-product formation during silicon film deposition using trichlorosilane gas was studied by two types of in situ measurement techniques, such as the langasite crystal microbalance (LCM) and the quadrupole mass spectra (QMS) analyzer, installed at the exhaust of the chemical vapor deposition (CVD) reactor. With the increasing hydrogen gas concentration, the QMS showed that the partial pressure related to SiCl₂ decreased. Simultaneously, the deposition on the LCM surface decreased. Because SiCl₂ gradually produces the burnable by-product of (SiCl₂)₉, an oily silane, at the exhaust, the CVD parameters effective for suppressing the SiCl₂ formation were evaluated.

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Semiconductor silicon film is a widely used material in various fields including microelectronics, solar cells and power electronics. In industry, trichlorosilane gas is quite often used for producing silicon films by means of chemical vapor deposition (CVD), because the very high purity trichlorosilane is widely available at a reasonable price, and because its storage and use are easier and safer than the other silicon precursors.

The silicon film deposition using chlorosilane gases has been studied for many years by various researchers. They mainly evaluated the chemical species and processes accounting for the deposition rate in order to improve the CVD processes and to design the CVD reactors. In a trichlorosilane-hydrogen system and in a cold wall system, trichlorosilane was shown to directly reach the silicon substrate surface for producing the silicon film. Additionally, the silicon deposition rate could be sufficiently described following an Eley-Rideal surface reaction model. Although SiCl₂ was shown to be produced by the thermal decomposition of trichlorosilane in the gas phase of the cold wall environment, its amount was shown to be too low to influence the film deposition rate.

However, from a different point of view for achieving a safe operation for the long-term use of the CVD reactor in industry, the by-product, called oily silane, must be taken care. After the repetitive CVD operation for a month or more, an enormous amount of oily silane often fills the exhaust tube. Thus, the exhaust tube is periodically cleaned. However, this operation has several problems. The cleaning operation requires several hours. Additionally, the oily silane is burnable and sometimes explodes. In order to avoid disastrous accidents, the conditions producing oily silane should be further studied relating to the SiCl₂ formation, because the oily silane has been identified as polymerized SiCl₂. (SiCl₂)₉, (in detail, X-(SiCl₂)₉-Y. X and Y are end groups). Additionally, when the silicon wafer diameter is enlarged from 300 mm to 450 mm in the future, the by-product problem will become more serious due to the huge consumption of the precursor.

Based on empirical information, keeping the exhaust warm is considered to be effective for decreasing the oily silane deposition. Additionally, from the viewpoint of equilibrium between chlorosilanes and ambient gases, hydrogen is expected to play some role in decreasing SiCl₂ in a chlorosilane-hydrogen system. Thus, the SiCl₂ formation should be studied in detail.

For this kind of study by an experimental approach, an in situ monitoring technique is convenient, such as using the quadrupole mass spectra (QMS) analyzer for the gas species analysis and the langasite crystal microbalance (LCM) for measuring a significantly slow deposition. The combination of these tools is expected to reveal significantly weak and slow phenomena, like the oily silane deposition.

In this study for evaluating the CVD parameters related to the SiCl₂ formation, the silicon film deposition was performed in a trichlorosilane-hydrogen system. The in situ monitoring techniques, such as the QMS and the LCM, were used. The relationship between the produced SiCl₂ amount and the hydrogen gas concentration was focused on.

Experimental

Fig. 1 shows the CVD reactor used in this study. Small silicon plates, having dimensions of 3 cm × 3 cm, were used as the substrate. This silicon substrate was the Czochralski-grown crystal with a (100) plane. The substrate was placed in the quartz chamber. The inner height and width of the quartz chamber was 1 cm and 4 cm, respectively.

The silicon substrate was heated using the infrared flux emitted from six halogen lamps placed on the top and bottom of the chamber. Trichlorosilane gas mixed with hydrogen and nitrogen gases was introduced to the chamber at atmospheric pressure. The total flow rate of the hydrogen and nitrogen was fixed at 1.05 slm. The hydrogen flow rate was 0.55, 0.85 and 1.05, while the nitrogen flow rate was 0.5, 0.2 and 0.0 slm. The TCS flow rate was 0.03 slm.

A part of the exhaust gas was fed to the QMS analyzer (PrismaPlus QMG220, Pfeiffer Vacuum, Germany). The exhaust flange attached at the end of the chamber had a connecting port to the LCM sensor. The photograph at the left bottom of Fig. 1 shows the LCM sensor (10 MHz, Halloran Electronics, Tokyo, Japan) which was installed in the exhaust flange. The frequency of the LCM sensor was monitored.

![Figure 1. Chemical vapor deposition reactor used in this study. The LCM and the QCM analyzer are installed at the exhaust.](image-url)
and displayed on the computer display. The temperature of the exhaust flange was less than 40 °C throughout the silicon film formation process.

Fig. 2 shows the CVD process performed in this study. The ambient gas was a mixture of high purity hydrogen gas and nitrogen gas (99.9999%, Simitomo Seika Kogyo, Tokyo Japan). Its total gas flow rate was 1.05 slm. The substrate was heated to 900 °C, which was measured using a thermocouple in ambient nitrogen before the deposition. After reaching a steady-state, trichlorosilane gas (Tri Chemical Laboratories, Inc., Yamanashi, Japan) was introduced at 0.03 slm for 5 min.

The overall chemical reaction is as follows:

\[ \text{SiHCl}_3 + H_2 \rightarrow \text{Si} + 3\text{HCl}. \]  

A silicon film and hydrogen chloride are produced by the reduction of trichlorosilane gas using hydrogen gas.

Fig. 3a shows the typical mass spectra by the QMS measurement in this study. At the mass of 2, hydrogen gas was detected. Because the partial pressure of hydrogen was the highest, the partial pressures of the other species were normalized using that of hydrogen. At the masses of 35, 36, 37 and 38, hydrogen chloride appeared. This was one of the products of the chemical reaction depicted by equation 1. At the masses near 63, 98 and 133, the SiCl\(^+\), SiCl\(_2\)\(^+\) and SiCl\(_3\)\(^+\) groups were observed, respectively. The SiCl\(_2\)\(^+\) group corresponds to trichlorosilane which was introduced from the inlet as the precursor. For the SiCl\(_3\)\(^+\) group, three kinds of assignments are possible, that is, SiCl\(_2\), dichlorosilane (SiH\(_2\)Cl\(_2\)) and fragments\(^{11,12}\) of the chlorosilanes. The SiCl\(_2\) molecules are produced by the thermal decomposition of trichlorosilane in the gas phase based on equation 2.

\[ \text{SiHCl}_3 \rightarrow \text{SiCl}_2 + \text{HCl}. \]  

Dichlorosilane may be produced in the gas phase following equilibrium between the various chlorosilanes.\(^{13}\) Because the mass of dichlorosilane is very near that of SiCl\(_2\), they are very difficult to be distinguished from each other. The fragments of the trichlorosilane molecules are produced only in the mass analyzer. Next, the SiCl\(_2\)\(^+\) group is considered to be the fragments of SiCl\(_2\), dichlorosilane and trichlorosilane. Taking into account the origins of the chlorosilane species observed by the QMS,\(^3\) both the SiCl\(_3\)\(^+\) group and SiCl\(_2\)\(^+\) group were considered to include SiCl\(_2\) in the gas phase. Thus, these two groups were taken into account for evaluating the SiCl\(_2\) production behavior in this study.

Fig. 3b shows a schematic of the LCM frequency behavior during the CVD process. When the steady-state was achieved in the CVD reactor, the value of LCM frequency was that at Step 0. By introducing the heavy precursor gas, like trichlorosilane having the molecular weight of 135.5, into the light ambient gas, such as hydrogen, the LCM frequency immediately decreased and became that at Step 1. This frequency shift is described using a simple equation accounting for the gas density and gas viscosity.\(^{14-16}\) After the frequency shift from Step 0 to Step 1, the LCM frequency gradually decreased corresponding to the weight increase caused by the deposition and reaches Step 2. By terminating the precursor gas supply, the LCM frequency immediately recovered to the higher value. The frequency then soon became a steady-state at Step 3. The LCM frequency differences between Step 0 and Step 3 were used for the evaluation of the by-product deposition on the LCM, because the difference between these two steps is only the weight on the LCM.

Results and Discussion

Fig. 4 shows the ratio of the chlorosilane groups obtained in this study using various combinations of hydrogen and nitrogen gas flow rates. This figure was obtained by taking the summation of the partial pressures belonging to each group, such as SiCl\(_3\)\(^+\), SiCl\(_2\)\(^+\) and SiCl\(_2\)\(^+\). In this figure, the white, dark and gray bars indicate the SiCl\(_3\)\(^+\), SiCl\(_2\)\(^+\) and SiCl\(_2\)\(^+\) groups, respectively. With the increasing hydrogen gas flow rate and the decreasing nitrogen gas flow rate, no significant change was recognized. While the SiCl\(_2\)\(^+\) group slightly increased from 48 to 53%, the SiCl\(_2\)\(^+\) group was near 40% (38–41%) and its change was negligible. In contrast, the slight decrease in the SiCl\(_2\)\(^+\) group, from 13 to 6%, could be recognized. Because the 5% increase in the SiCl\(_2\)\(^+\) group was comparable to the 7% decrease in the SiCl\(_3\)\(^+\) group, the increase in the hydrogen concentration was considered to play a role in decreasing the SiCl\(_3\) production in the gas phase.

Next, the typical behavior of the LCM frequency set at the exhaust is shown in Fig. 5. In this measurement, the silicon substrate was heated from room temperature to 900 °C in ambient hydrogen. During the heating, the LCM frequency decreased to −400 Hz corresponding to its temperature change within ten degrees. After reaching the steady-state, trichlorosilane gas was introduced at Step 0. Although the LCM frequency showed a quick up and down, it soon plateaued near −600 Hz at Step 1. Additionally, the LCM frequency gradually decreased from Step 1 to Step 2, because of the by-product deposition. Through this, the LCM frequency decreased about 100 Hz for 5 min. At Step 2, the trichlorosilane gas supply was terminated. The LCM frequency increased to the value of ambient hydrogen at Step 3. i.e. near −600 Hz. After reaching a steady-state, the heating was turned off. Due to the cooling to room temperature, the LCM frequency immediately decreased and became that at Step 1. This frequency shift is described using a simple equation accounting for the gas density and gas viscosity. After the frequency shift from Step 1 to Step 2, the LCM frequency gradually decreased corresponding to the weight increase caused by the deposition and reaches Step 2. By terminating the precursor gas supply, the LCM frequency immediately recovered to the higher value. The frequency then soon became a steady-state at Step 3. The LCM frequency differences between Step 0 and Step 3 were used for the evaluation of the by-product deposition on the LCM, because the difference between these two steps is only the weight on the LCM.
The symbol * indicates that the species is chemisorbed at the surface. Path (a) is the chemisorption of *SiCl₂ at the silicon surface and desorption of hydrogen chloride from the silicon surface. Path (b) is simply transformed from the frequency shift using equation 3 in the by-product deposition at the LCM sensor surface.

Fig. 6 shows the weight change at Step 3 from Step 0. This value was simply transformed from the frequency shift using equation 3 in this study.

Weight increase (ng cm⁻²) = Frequency shift (Hz) × 1.47.  [3]

Fig. 6 clearly shows that the weight increase at the LCM surface decreased with the increasing hydrogen gas concentration, while the trichlorosilane gas concentration was fixed at 2.9%. Because the thickness of the deposited by-product was quite thin, any change in appearance of the LCM sensor surface could not be recognized by visual inspection. However, by considering the relationship between the results from the LCM and the QMS, the by-product deposition related to SiCl₂ that is, the oily silane formation, could be suppressed by the hydrogen gas concentration.

For the last part of this study, the chemical reactions causing the SiCl₂ production are discussed in detail using Fig. 7. The dominant process for the silicon film deposition is Paths (a) and (b).  

Path (a): SiHCl₃ → *SiCl₂ + HCl  [4]

Path (b): *SiCl₂ + H₂ → Si + 2HCl  [5]

The symbol * indicates that the species is chemisorbed at the surface.

Path (a) is the chemisorption of *SiCl₂ at the silicon surface and desorption of hydrogen chloride from the silicon surface. Path (b) is the silicon film production due to the reduction of *SiCl₂ using hydrogen.

*SiCl₂ can be desorbed from the silicon surface.  [17]

Path (c): *SiCl₂ → SiCl₂ in gas phase.  [6]

Paths (d) - (g) occur in the gas phase, as shown in Fig. 7. Trichlorosilane is thermally decomposed to produce SiCl₂ and hydrogen chloride in the gas phase, following Path (d), written as equation 7.

Path (d): SiHCl₃ → SiCl₂ + HCl  [7]

SiCl₂ can combine with itself to form large molecules, (SiCl₂)ₙ, in the gas phase, following Path (e), as described by equation 8. When n is high, (SiCl₂)ₙ is adsorbed at the LCM surface, the temperature of which is significantly lower than those of the silicon substrate and the gas phase in the chamber. This process follows Path (f), written as equation 9. When n is not high, (SiCl₂)ₙ is transported to the QMS analyzer through the exhaust tube, as Path (g), in equation 10.

Path (e): nSiCl₂ → (SiCl₂)ₙ  [8]

Path (f): (SiCl₂)ₙ (n: large) → (SiCl₂)ₙ on LCM.  [9]

Path (g): (SiCl₂)ₙ (n: 1 or small) → (SiCl₂)ₙ to QMS analyzer.  [10]

In the gas phase, SiCl₂ reacts with hydrogen to produce dichlorosilane, following Path (h), described by equation 11.

Path (h): SiCl₂ + H₂ → SiH₂Cl₂.  [11]

Because dichlorosilane has a high vapor pressure, it is transported to the QMS analyzer, following Path (i), written as equation 12. Simultaneously, the large amount of trichlorosilane is directly transported to the QMS analyzer, following Path (j), written as equation 13.

Path (i): SiH₂Cl₂ to QMS.  [12]

Path (j): SiHCl₃ → SiHCl₃ to QMS.  [13]

Next, the role of hydrogen gas is evaluated following the rate theory.  [4]

The rate of Path (a), V(α), is expressed as follows:

\[ V(\alpha) = k(\alpha)(1 - \Theta)[\text{SiHCl}_3] \]  [14]

where \( k(\alpha) \) is the rate constant for Path (α), \( \Theta \) is the coverage of the silicon surface by SiCl₂, and [SiHCl₃] is the trichlorosilane gas concentration at the silicon surface. Although hydrogen gas does not influence Path (a), it enhances the rate of silicon film production by Path (b), as described by equation 15.

\[ V(b) = k(b) \Theta[H_2], \]  [15]
where \( V_{(b)} \) is the rate of Path (b), \( k_{(b)} \) is the rate constant for Path (b), and [H\(_2\)] is the hydrogen gas concentration at the silicon surface. Previous studies\(^1\)\(^-\)\(^2\)\(^\dagger\) showed that Path (b) is the rate limiting process for the industrial silicon epitaxial film deposition. The SiCl\(_2\) desorption rate, \( V_{(c)} \), is described by equation 16.

\[
V_{(c)} = k_{(c)} \Theta,
\]

where \( k_{(c)} \) is the SiCl\(_2\) desorption rate constant. From equations 14, 15 and 16, the SiCl\(_2\) chemisorption rate is equal to the summation of the Si film formation rate and the SiCl\(_2\) desorption rate as follows:

\[
V_{(a)} = V_{(b)} + V_{(c)}.
\]

By this relationship, the surface coverage is obtained.

\[
\Theta = \frac{k_{(a)} \text{[SiHCl\(_3\)]}}{k_{(a)} \text{[SiHCl\(_3\)]} + k_{(b)} \text{[H\(_2\)]} + k_{(c)}},
\]

Using equation 18, the SiCl\(_2\) desorption rate is described as follows:

\[
V_{(c)} = \frac{k_{(a)} k_{(c)} \text{[SiHCl\(_3\)]}}{k_{(a)} \text{[SiHCl\(_3\)]} + k_{(b)} \text{[H\(_2\)]} + k_{(c)}}.
\]

Thus, the SiCl\(_2\) desorption rate, \( V_{(c)} \), is expected to be decreased by the increasing hydrogen gas concentration, following equation 19. This trend agrees with the measurements.

Next, the SiCl\(_2\) production in the gas phase is discussed. Because Path (d) is a thermal process, it spontaneously occurs depending on the gas phase temperature and does not depend on the hydrogen gas concentration. Additionally, the production and polymerization rates of SiCl\(_2\), Paths (d) – (g), do not depend on the hydrogen gas concentration. Similarly, the rates of Paths (i) and (j) are not a function of the gas phase temperature. For example, the rate constant near 1200 K becomes nearly 1/10 times lower value by means of 50 degrees decrease in the gas phase temperature.

In conclusion, the decrease in Paths (c) and (d) with the increase in Path (h) is expected to help decrease the SiCl\(_2\) and the subsequent oily silane production at the exhaust. The other conclusion is that the LCM sensor is a quite useful tool, because it could quickly detect the change, which was too low to be detected by the other measurement tool.

### Conclusions

The formation of byproducts caused from trichlorosilane during the silicon film deposition was studied. Two kinds of in situ monitors, such as the LCM and the QMS analyzer, were installed at the exhaust of the CVD reactor and were used for the by-product behavior analysis. With the increasing hydrogen gas concentration, the partial pressure related to the species of SiCl\(_2\) decreased in the QMS. Simultaneously, the deposition on the LCM surface decreased. These results indicated that the SiCl\(_2\) molecules produced in the gas phase and at the silicon surface reacted with each other to form (SiCl\(_2\))\(_n\), which was the form of oily silane. In order to suppress the SiCl\(_2\) formation, increasing the hydrogen gas concentration and decreasing the gas phase temperature are important methods. Based on this study, the LCM sensor was additionally shown to have the capability of studying the very slow and small but important process, such as the by-product production in a trichlorosilane-hydrogen system.

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### References

1. D. J. Meyer, Electrochem. Soc., Proc., 2005–06, 81 (2005).
2. S. Koomu, G. M. Wilson, and Banim Khomami, J. Electrochem. Soc., 147(4) 1538 (2000).
3. A. Veneroni, D. Moscattelli, and M. Masi, J. Crystal Growth, 275, e289 (2005).
4. H. Habuka, T. Nagoya, M. Mayusumi, M. Katayama, M. Shimada, and K. Okuyama, J. Cryst. Growth, 169, 61 (1996).
5. H. Habuka, Y. Aoyama, S. Akiyama, T. Otsuka, W. F. Qu, M. Shimada, and K. Okuyama, J. Crystal Growth, 207, 77 (1999).
6. Japan patent Kokai No. 2013-045799.
7. https://www.mmc.co.jp/coporate/ja/01/01/14-0612.html [in Japanese].
8. P. Comita, D. Carlson, Y. Cheng, K. Klimck, A. Waldhauer, and R. Ranganathan, Chemical Vapor Deposition, Ed: M. D. Allendorf and C. Berbard, Electrochem. Soc. Proc., 97–25, 684 (1997).
9. http://www.appliedmaterials.com/ja.
10. H. Habuka and K. Kote, Jpn. J. Appl. Phys., 50, 096505 (2011).
11. T. E. Lee, A Beginner’s Guide to Mass Spectral Interpretation (Wiley, Chichester, 1998).
12. J. R. Chapman, Practical Organic Mass Spectroscopy (Wiley, Chichester, 1993).
13. Silicon Epitaxy, Ed. D. Crippa, D. L. Rode, and M. Masi (Academic Press, San Diego, USA, 2001).
14. H. Habuka and Y. Tanaka, ECS J. Solid State Sci. Technol., 1, 62 (2012).
15. H. Habuka and Y. Tanaka, J. Surf. Eng. Mater. Adv. Technol., 3, 61 (2013).
16. H. Habuka and M. Matsui, Surf. Coat. Technol., 230, 312 (2013).
17. G. A. de Wijs, A. De Vita, and A. Selloni, Phys. Rev. Lett., 78, 4877 (1997).
18. H. Habuka, J. Suzuki, Y. Takai, H. Hirata, and S. Mitani, J. Cryst. Growth, 327, 1 (2011).
19. M.-D. Su and H. B. Schlegel, J. Phys. Chem., 97, 9981 (1993).