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Surface and gas phase reactions induced in a trichlorosilane–SiH_x system for silicon film deposition

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ABSTRACT

The surface and gas phase reactions caused by trichlorosilane and SiH_x in ambient hydrogen were studied in order to improve the silicon film deposition process. The concentration of trichlorosilane exhausted from the reactor was measured by a quadrupole mass spectra analyzer. Simultaneously, the byproduct deposition that occurred at the exhaust was measured by a quartz crystal microbalance. Based on the measurements, SiH_x is considered to increase the trichlorosilane consumption efficiency and to decrease the $SiCl_2$ production by increasing the silicon formation rate from the surface intermediate species, $SiCl_2$. Additionally, trichlorosilane and hydrogen were considered to be reproduced from SiH_x and the hydrogen chloride caused by the silicon film formation.

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1. Introduction

Semiconductor silicon film is produced by chemical vapor deposition (CVD), for fabricating various electronic devices, such as microprocessors, memories, solar cells and power transistors. For the silicon film deposition, one of the most frequently-used silicon precursors in the industry is trichlorosilane ($SiHCl_3$, TCS) [1–3], because of its very high purity, reasonable cost and ease of use.

For producing the silicon film having a uniform thickness on a large diameter substrate, such as a 300 and 450 mm-diameter wafer, using trichlorosilane gas, there are some issues to be solved. One of them is the low consumption efficiency of the trichlorosilane. In order to achieve a uniform distribution of the trichlorosilane concentration over the substrate surface, a very high amount of trichlorosilane is often supplied to the reactor. However, the trichlorosilane consumption efficiency tends to decrease. Additionally, the formation of byproducts, such as oily silane, typically $(SiCl_2)_n$ [4,5], unfortunately increases. The oily silane has been empirically known to be explosive and to often cause serious accidents losing human lives [6]. In order to increase the trichlorosilane consumption rate and to decrease the byproduct formation [5], a new chemical process should be studied by adding any reactive species. This approach is possible as an extension of our previous study [5] for trichlorosilane–hydrogen system.

The silicon epitaxial growth rate in the trichlorosilane–hydrogen system is governed by the surface concentration of the intermediate species, $SiCl_2$ [7]. Even if the trichlorosilane gas was sufficiently supplied, the growth rate becomes saturated and is governed only by the hydrogen concentration at the surface [8]. The hydrogen concentration is not easily increased from that at atmospheric pressure. In order to exceed the saturated growth rate due to its own surface chemical mechanism, alternative or additional chemical paths at the silicon surface and in the gas phase are expected.

For this purpose, the gas mixture of chlorosilanes and silanes [9–11] is one of the possible candidates, because the silanes are very reactive. If silanes work as an accelerator of the trichlorosilane chemical reactions, the growth rate is expected to exceed the saturated value. For studying the chemical process, the rate limiting process should be again discussed and evaluated in detail, taking into account several notable previous studies [12–14].

In this study, the effect of SiH_x ($x = 1$–3) on the trichlorosilane consumption efficiency was experimentally evaluated by means of the gas concentration analysis using a quadrupole mass spectra analyzer (QMS). Additionally, the amount of byproduct deposition was measured using a quartz crystal microbalance (QCM). Based on the measurements, the chemical reaction paths at the surface and in the gas phase are discussed in detail. Monomethylsilane (SiH_3CH_3, MMS) gas was used for safely producing the SiH_x in the gas phase by thermal decomposition [15,16].

2. 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. The silicon substrate was a Czochralski-grown crystal having a (100) plane. The substrate was placed in the quartz chamber. The inner height and width of the quartz chamber were 1 cm and 4 cm, respectively.

The silicon substrate was heated using the infrared flux emitted from six halogen lamps placed at the top and bottom of the chamber. Trichlorosilane gas and monomethylsilane gas diluted with hydrogen

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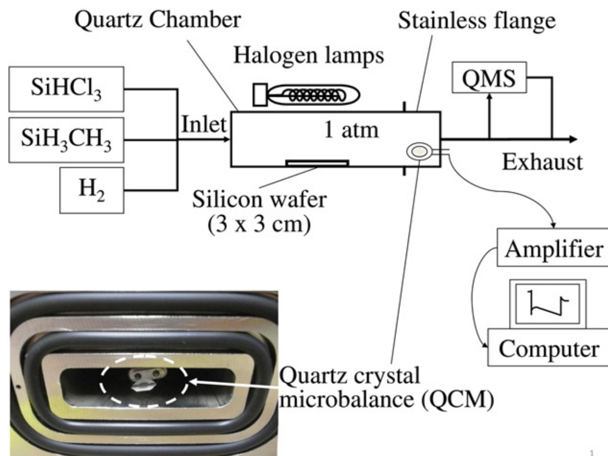

Fig. 1. Chemical vapor deposition reactor along with quadrupole mass spectra analyzer and quartz crystal microbalance.

gas were introduced into the chamber at atmospheric pressure. The flow rate of hydrogen was fixed at 1.05 slm. The monomethylsilane gas flow rate was 0–0.025 slm, while the trichlorosilane flow rate was fixed at 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 QCM sensor (10 MHz, 0.5 ng/(cm^2 Hz), Halloran Electronics, Tokyo Japan), which is shown in the photograph at the left bottom of Fig. 1. This sensor has a sufficient sensitivity to detect any small weight change [17] less than that of the silicon monolayer deposition. The frequency of the QCM sensor was monitored and displayed on the computer. The temperature of the exhaust flange was kept lower than 40 °C through the silicon film formation process.

Fig. 2 shows the typical CVD process used in this study. The ambient gas was high purity hydrogen gas (99.9999%, Simitomo Seika Kogyo, Tokyo, Japan). Its gas flow rate was 1.05 slm. The substrate was heated to 950 °C, which was measured using a thermocouple in ambient nitrogen before the deposition. After reaching a steady state, the trichlorosilane gas and monomethylsilane gas (Tri Chemical Laboratories, Inc., Yamanashi, Japan) were introduced at the same time for 7 min. The thermal decomposition of the monomethylsilane gas [15, 16] was utilized for safely producing SiH_x. Trichlorosilane has the following dominant overall chemical reaction [7]:

$$SiHCl_3 + H_2 \rightarrow Si + 3HCl. \quad (1)$$

The concentration of trichlorosilane at the exhaust was measured by the QMS in order to obtain the influence of SiH_x gas on the trichlorosilane gas consumption.

Although the cold wall condition of the reactor is preferred for the industrial silicon epitaxial growth, the hot wall condition was used in this study in order to clearly recognize the occurrence of any possible reactions. Although the measurement was often scattered for such conditions, the overall qualitative trend could be obtained.

The silicon deposition rate at the temperatures near 900 °C increased to 30–40% higher values by means of adding a very small amount of monomethylsilane gas. The deposition rate will be reported elsewhere, in detail. Thus, this study focuses on the chemical processes.

3. Results and discussion

3.1. Mass spectra

Fig. 3 shows the quadrupole mass spectra, which showed the various chemical species contained in the gas exhausted from the reactor. The ambient hydrogen gas was detected at the mass of 2. The masses near 133 showed the $SiCl_3^+$ group, corresponding to trichlorosilane. Chlorosilanes simultaneously appeared near 63 and 98, corresponding to the $SiCl^+$ group and $SiCl_2^+$ group, respectively. The $SiCl_4^+$ group was also observed near 168. The masses at 35–38 clearly showed the existence of hydrogen chloride which was produced from the trichlorosilane based on Eq. (1).

Monomethylsilane was detected at the masses higher than 40. Additionally, the monomethylsilane was recognized to be thermally decomposed due to the existence of the CH_3^+ group near 12 and that of the SiH_3^+ group near 28.

The small peaks at the masses near 110 correspond to $SiHCl_2CH_3$, which was expected to be produced by the reaction between monomethylsilane and hydrogen chloride in the gas phase. Those near 80 could be assigned to SiH_2ClCH_3.

3.2. Gas concentrations and byproduct deposition

Figs. 4, 5 and 6 show the measurement by the QMS analyzer and the QCM. Fig. 4 shows the partial pressure of the $SiCl_3^+$ group which showed the amount of trichlorosilane gas exhausted from the CVD reactor. In this figure, plots of the trichlorosilane gas concentration distributed only in the left bottom region. The solid line shows the highest values of this measurement. Any scattering plots were distributed in the region under this line. The highest values of the trichlorosilane gas concentration indicated the trend that the consumption of trichlorosilane gas increased with the increasing monomethylsilane gas concentration, even for the cases having the lowest consumption rate at each monomethylsilane concentration.

Fig. 5 shows the partial pressure of hydrogen chloride gas measured at the exhaust. Plots in this figure also had a large scatter with an unclear trend. The solid line shows the trend expected from the highest values of the hydrogen chloride partial pressure, similar to Fig. 4. From Fig. 5, the highest amount of hydrogen chloride gas was considered to be moderately increased with the increasing monomethylsilane gas.

The deposited byproduct amount caused by the chemical reactions in the chamber was measured using the QCM, as shown in Fig. 6. The solid line shows the highest amount of the byproduct deposition.

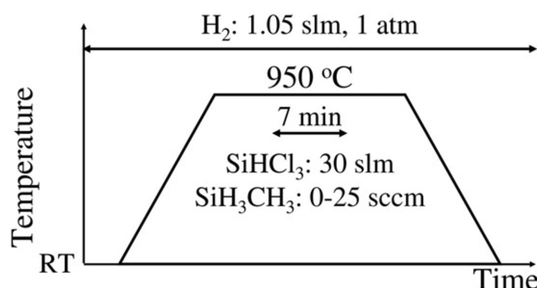

Fig. 2. Chemical vapor deposition process in this study.

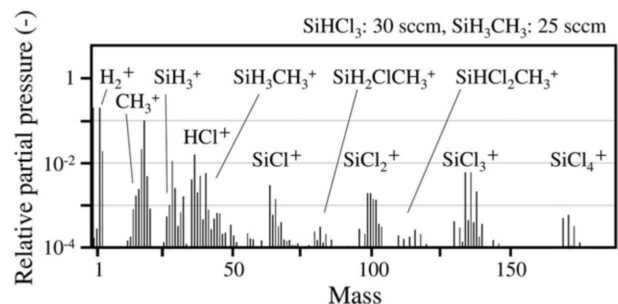

Fig. 3. Quadrupole mass spectra measured at exhaust of chemical vapor deposition reactor using trichlorosilane and monomethylsilane gases in ambient hydrogen.

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