

The Surface Reaction Rate for Silane on Polycrystalline Silicon Obtained by Using a Fast Wafer-Rotating Reactor

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The surface reaction rate for silane on polycrystalline silicon was determined to be between 800-900°C at growth pressure of 38 Torr with hydrogen by using a fast wafer-rotating reactor. The growth rate dependence on silane partial pressure was varied with the rotation speed because of the change of the gas phase reaction. The actual reaction order for the silane partial pressure on a wafer was determined to be 0.67, in which the influence of reaction intermediates for film growth was excluded by using a simulation result. This value was different from previously reported values. The surface reaction model was also discussed.

1 Introduction

Clarification of the surface reaction mechanism in CVD processes is necessary for growth rate simulation in CVD reactors, especially in the case of polycrystalline silicon growth, since the surface reaction rate dominantly affects the growth rate. Furthermore, growth conditions are optimized more easily as the surface reaction mechanism is clarified. However, it is difficult to separate the individual surface reaction rates of both source materials and the reaction intermediates produced in a reactor, because the concentration of the individual intermediates on a wafer is difficult to determine. The authors carried out the growth of polycrystalline silicon by using a fast wafer-rotating reactor, and have determined the surface reaction rate for silane from the calculated value of silane partial pressure on a wafer. The surface reaction order for silane has been found to be 0.67, which is different from previously reported values of 0.5 of 1¹⁾.

2 Experiment

The growth rate dependence on the silane gas flow rate was examined at the wafer temperature of 800°C under wafer rotation speeds of 1200 and 10800 rpm using a fast wafer-rotating reactor²⁾. The reactor diagram is shown in Fig.1. The growth condition is summarized in Table 1.

3 Growth results

Arrhenius plots of the growth rate are

shown in Fig.2. The growth was surface reaction controlled between 800-900°C under both rotation speeds. The apparent activation energy changed with the rotation speed, which suggests that the gas species contributing to film growth changed.

Figure 3 shows the growth rate dependence on the silane gas flow rate at 800°C. The growth rate was not proportional to the silane flow rate. The growth rate at 1200 rpm was faster than that at 10800 rpm. The growth rate in Fig.3 is plotted versus silane partial pressure in Fig.4. The reaction order was 0.79 and 0.69 at 1200 and 10800 rpm, respectively, which also suggests a change in the species.

The silane contribution ratio to growth is considered to be larger at 10800 rpm than at 1200 rpm, since a higher rotation speed suppresses the gas phase reactions in a fast wafer-rotating reactor²⁾.

4 Calculation of surface reaction rate

The authors intended to extract the surface reaction of silane from the growth results, since silane surface concentration and the ratio of silane contribution to the growth rate can be determined from the calculation of silane diffusion and reactions under an infinite disk rotation induced flow²⁾, by using fluid properties at arithmetic mean temperature at an inlet and a wafer. In the calculation, it was assumed that silane thermally decomposes into silylene, and both silane and silylene contribute to film growth, as shown in Fig.5. The gas phase reaction rate constant was taken from the work of Coltrin et al.³⁾ by assuming its linear dependence on the pressure. The

sticking probability of silylene was assumed to be unity. Under the assumption of the surface reaction rate of silane, which was the boundary condition for the calculation, the silane concentration profile above the wafer and the growth rate can be determined. The form of silane surface reaction rate was assumed to be

$$G.R. = k_s p_s^\alpha, \quad (1)$$

where p_s is the silane partial pressure on a wafer, k_s is the rate constant, and α is the reaction order and was determined self-consistently, and was found to be 0.67, although reported values of α have been 0.5 or 1¹⁾. The growth rate was expressed as

$$G.R. = 2.67 \exp\left(-\frac{20300}{T}\right) p_s^{0.67}, \quad (2)$$

where G.R. is the growth rate in $\mu\text{m}/\text{min}$, T is the temperature in K and p_s is the silane partial pressure in Torr. The bold lines in Fig.3 indicate the simulation results in which the surface reaction rate expressed by Eq.2 was used. The growth rate dependence on both the silane flow rate and the rotation speed was well explained by the model.

The surface concentration of silane non-dimensionalized by the inlet concentration is shown in Fig.6 as a function of the silane gas flow rate. The surface concentration of silane was almost the same as the inlet concentration at 10800 rpm, while that was small at 1200 rpm due to the gas phase decomposition reaction. The contribution ratio of silane for the growth is shown in Fig.7 as a function of the silane gas flow rate. The silane contribution ratio for growth was not unity even at 10800 rpm because of the higher reactivity of low concentration silylene.

5 Discussion

The rate-determining step for film growth depends on the growth condition. The activation energy reflects the rate-determining step, and the reaction order reflects the reaction mechanism such as adsorption, desorption, etc. The relatively high activation energy of 40 kcal/mol indicated that the surface reaction such as adsorbed silane decomposition reaction was the rate-determining step and that the desorption of hydrogen, which is reported to affect the growth rate was not it. The reaction order of 0.67 appears to indicate that the adsorption of silane was the Freundlich type of adsorption isotherm;

$$\text{SiH}_4^* \propto p_{\text{SiH}_4}^{\frac{1}{n}}, \quad (3)$$

where SiH_4^* denotes the adsorbed silane and n is the constant. From the experimental results,

n appears to equal 1.5 or 3 dependent on the reaction order of the rate-determining step on the wafer; i.e., 1.5 for the unimolecular reaction and 3 for the bimolecular reaction. The reported reaction order was measured in a conventional batch type LPCVD reactor. Therefore, exact reaction order for silane could not be obtained, since the reaction intermediate, the reaction order of which could be unity, affects the growth rate.

The growth rate is also obtained by sticking probability for silane measured by the molecular beam method⁴⁾. In this case, the surface condition of the wafer is different from that under the reduced hydrogen condition, and the internal energy state of silane, which is determined by the silane temperature, is also different. The fast wafer-rotating reactor offers the surface reaction analyzing method applicable to an actual growth surface and a thermally activated source material.

5 Conclusion

The surface reaction rate for silane on polycrystalline silicon has been determined by using a fast wafer-rotating method. The growth rate dependence on the silane partial pressure and the temperature has been found to be

$$G.R. = 2.67 \exp\left(-\frac{20300}{T}\right) p_s^{0.67},$$

where G.R. is the growth rate in $\mu\text{m}/\text{min}$, T is the temperature in K and p_s is the silane partial pressure in Torr. The reaction order of silane has been found to be different from previously reported reaction orders.

References

- 1) Ch. Hopfmann et al., Appl. Surf. Sci. 52(1991)169.
- 2) Y. Sato et al., SSDM '92, (1992)20.
- 3) M. Coltrin et al., J. Electrochem. Soc. 136(1989)819.
- 4) R. Buss et al., J. Appl. Phys. 63(1988)2808

Table 1 Growth condition

Silane flow rate :	0.025-4 l/min
Hydrogen flow rate :	15 l/min
Wafer temperature :	800-1200 °C
Growth pressure :	38 Torr
Wafer rotation speed :	1200-10800 rpm
Wafer :	3" Si (111)

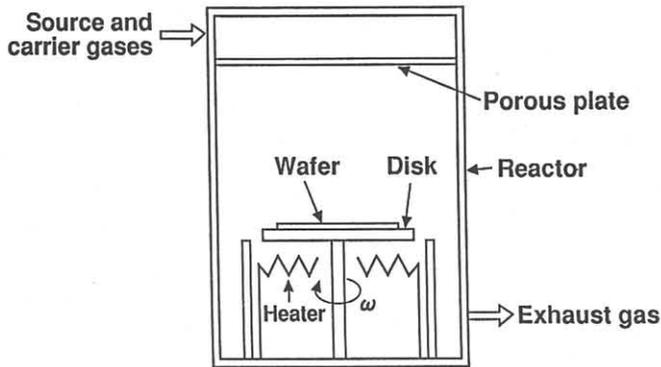


Fig.1 Schematic diagram of reactor

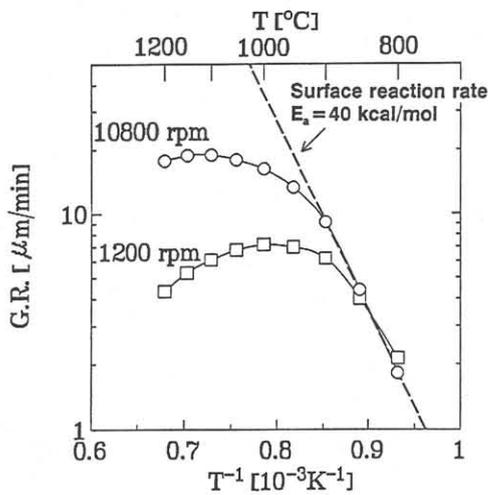


Fig.2 Growth rate dependence on Temperature
 $P=38$ Torr, $H_2=15$ l/min, $SiH_4=1$ l/min

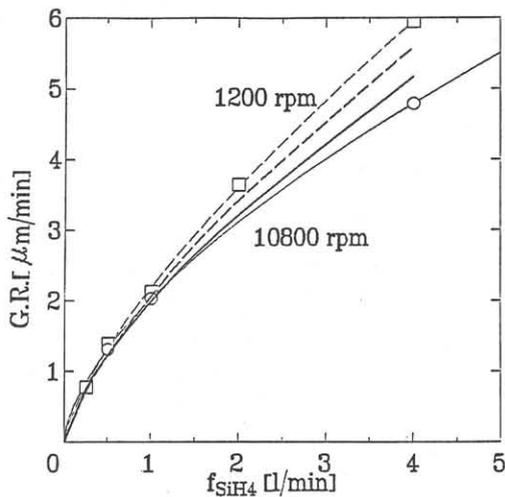


Fig.3 Growth rate dependence on silane flow rate
 $T=800$ °C, $P=38$ Torr, $H_2=15$ l/min

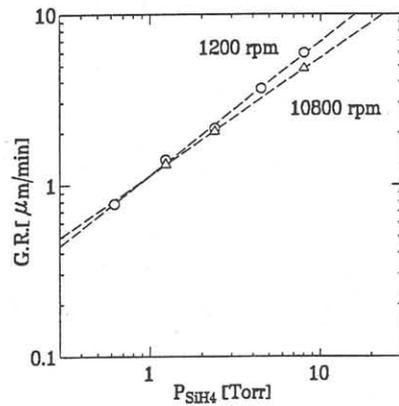


Fig.4 Growth rate dependence on silane partial pressure

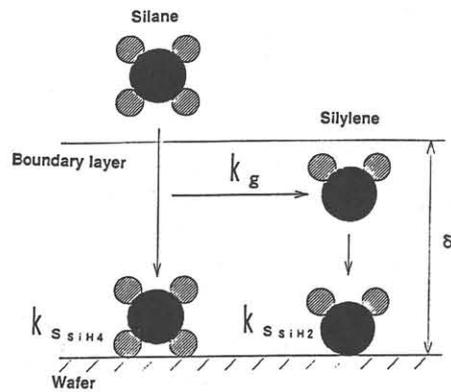


Fig.5 Silane reaction model

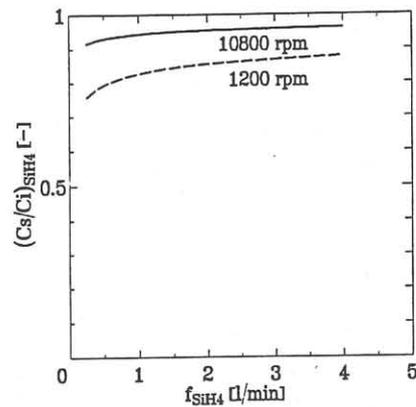


Fig.6 Surface concentration dependence on silane flow rate

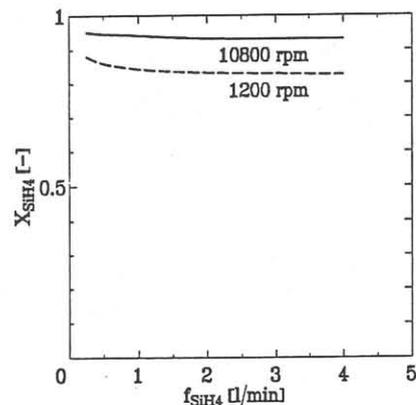


Fig.7 Contribution ratio of silane for growth dependence on silane flow rate