Silicon Molecular Layer Epitaxy

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ABSTRACT

This paper reports on recent results of silicon molecular layer epitaxy (MLE) using SiH₂Cl₂ and hydrogen. Growth conditions for monomolecular layers by the monomolecular layer deposition process have been investigated as a function of substrate temperature, pressure in the growth chamber, gas injection time, and vacuum evacuation time. The substrate temperature of 825°C was best suited to the monomolecular layer growth where the film thickness per cycle is saturated with the SiH₂Cl₂ injection pressure. From the results obtained by mass spectrometry and IR spectroscopy, we may con-clude that in the MLE growth the most predominant surface-adsorbed migrating species on silicon is SiCl₂. Also, the autodoping profiles of boron and other impurities have been measured by SIMS.

Suntola (1) has proposed the technique of atomic layer epitaxy (ALE) based on two methods: one is the alternate deposition of a monoatomic layer of a constituent element and that of another element; the other is to react the monomolecular layers adsorbed by the alternate injection of molecules of a molecular compound. As the second method is closely related to molecular surface reactions, we would prefer to designate it as molecular layer epitaxy (MLE). In the first method of ALE it is necessary to detect the formation of a monoatomic layer by electron diffraction, while in the second method the formation of the first monomolecular adsorbed layer is relatively stable in a rather wide range of temperature and pressure and the formation of the second and third adsorbed layers requires a considerably higher pressure. In the MLE growth, however, the desirable thickness of the monomolecular layer can be obtained without using expensive detection systems.

Another advantage of MLE is the relatively weak adsorption bonding between the adsorbed migrating species and the substrate. Especially, in the case of an organometallic compound, removal of the organic molecule after sticking of the migrated adsorbate to the kink or step is also rather easy; therefore, MLE by organometallic molecules is very attractive as the low temperature process.

In the case of silicon epitaxy, at first the experiment was carried out by use of SiH₂Cl₂; for the fundamental process is thought to be from previous experimental results (2)

$$SiH_2Cl_2 \rightarrow SiCl_2 \rightarrow Si$$
 [1]

and from the results of infrared spectroscopy (2, 3) the backetch by the produced HCl can be expressed as

$$Si + HCl \rightarrow SiCl_2 \text{ or } SiCl_3$$
 [2]

and

 $Si + Cl_2 \rightarrow SiCl_2 \text{ or } SiCl_3$ [3]

Experimental Setup

Figure 1 shows the experimental setup. This setup consists of a growth chamber, a gas injection control system of SiH₂Cl₂ and hydrogen, a heating IR lamp system, a temperature control unit with a pyrometer, a loading chamber,

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a quadrupole mass spectrometer, and a vacuum pumping system with a turbomolecular pump.

A silicon wafer with a (100) surface was used as the substrate. The wafer was cleaned in H₂SO₄: H₂O₂ solution and HCl:H₂O₂ solution and subsequently subjected to light etching of natural oxide in HF solution. After these treatments, the substrate was introduced into the loading chamber, which was evacuated to 1×10^{-4} Pa and was transferred to the growth chamber, and then the growth chamber was evacuated to 5×10^{-8} Pa. Then the substrate was heated by the IR lamp situated outside of the growth chamber, and the substrate temperature was measured by the pyrometer, whose output signal was coupled to the controlling unit at the lamp power.

Prior to growing the films, the surface of the substrate was cleaned in hydrogen at a temperature of 900°C for 600s. The growth chamber was then evacuated again and the substrate temperature was adjusted to the growth condition range of 775°-890°C. First, SiH₂Cl₂ was injected for 5



Fig. 1. Experimental setup

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Fig. 2. A pressure vs. time plot in the growth chamber during the gas injection. In this case, SiH_2CI_2 is injected for 40s and evacuated for 3s, then hydrogen is injected for 10s and evacuated for 7s.

to 50s at the pressures of 10^{-1} to 10^{-3} Pa and evacuated. Then hydrogen was injected for 0 to 15s at the pressures of 0 to 3×10^{-3} Pa and evacuated again. Such a periodic gas injection was repeated until the desired film thickness was obtained. Figure 2 shows a representative gas injection and evacuation time mode in this experiment. In Fig. 2. SiH₂Cl₂ is injected for 40s and evacuated for 3s, and the hydrogen is injected for 10s and evacuated for 7s. The gas injection and evacuation time mode will hereafter be described as (40", 3", 10", 7").

Results and Discussion

The film thicknesses per cycle as a function of the injected SiH_2Cl_2 pressure were measured with three different gas injection and evacuation time modes such as mode A (20", 3", 5", 7"), mode B (10", 3", 5", 7"), and mode C (5", 2", 3", 5").

In Fig. 3, the thickness of the grown film per cycle is a function of the injection pressure of SiH_2Cl_2 , at the substrate temperatures of 825° and $850^{\circ}C$. At each temperature, in a certain pressure range monomolecular layer growth takes place. When only SiH_2Cl_2 was injected for 20s without H_2 injection and evacuation for 7s, the monomolecular layer growth is never realized. However, in the higher pressure range, a relatively high speed multilayer growth can be observed, which roughly coincides with the SiH_2Cl_2 injection followed by H_2 injection at the same temperature. Then, the higher speed growth rate over a higher pressure range seems to be due to the self-deposition of SiH_2Cl_2 regardless of the injection of hydrogen. This can be expressed in the form

$$SiH_2Cl_2 \rightarrow Si + 2HCl$$
 [4]

or

$$SiH_2Cl_2 \rightarrow Si + H_2 + Cl_2$$
 [5]

If the injection time is 10 or 5s, the monomolecular growth rate can be kept constant even in the higher pressure range as shown in Fig. 3.

Therefore, the above phenomenon may be explained by decomposition of the adsorbed species stepwise: in a first step, the adsorbed SiH_2Cl_2 decomposes into $SiCl_2$, and in a second step, into Si. This seems to correspond to the result that the decomposition into silicon in the higher pressure range is enhanced at a high temperature of 850°C as shown in Fig. 3. This can be supported by the desorption QMS experiment which will be shown in Fig. 20.

Figure 4 shows the surface morphology by SEM, in which the surface morphology becomes impaired with decreasing injecting time of SiH_2Cl_2 from 20 to 5s. Therefore, sufficient surface migration or decomposition time seems very important to obtain perfect crystal morphology. Even in the case of mode C (5", 2", 3", 5"), however, electron beam diffraction reveals single-crystal growth as shown in Fig. 5.



Fig. 3. Growth rate of silicon film per cycle as a function of SiH₂Cl₂ injection pressure; SiH₂Cl₂ injection 20s, evacuation 3s, hydrogen injection 5s, and evacuation 7s. This is called mode A and represented by (20", 3", 5", 7"). Mode B (10", 3", 5", 7") and mode C (5", 2", 3", 5") are also included. The open circles represent the growth rates in the case of only SiH₂Cl₂ injection for 20s and evacuation for 7s (20", 7").

Infrared beam transmission experiments carried out by Nishizawa and co-workers (4-6) provided a great deal of experimental information about thermal dissociations of silane compounds; and Nihira (5) and Saito (6) observed chemical fluorescence light emission on silicon substrates



Fig. 4. SEM microphotographs of the epitaxial film surfaces grown under monomolecular layer conditions. The layers were grown at 825°C and at different pressures.



Fig. 5. Electron beam diffraction patterns of the surfaces of the crystal films grown in modes A and B. A similar pattern is obtained in mode C growth. These patterns show single-crystal film growth.

using SiCl₂ and SiCl₃, respectively. The former demonstrated that SiCl₂ is closely related to the final reaction in the growth of silicon, and the latter, SiCl₃ to the backetching of silicon. In 1975, Sedgwick (7) and Ban (8) reported the same results by Raman laser spectroscopy and QMS, respectively. But the above measurements were all carried out in the vicinity of the silicon surface and not on the adsorbate on it.

As shown in Fig. 6, the absorption by SiHCl₃ and SiH₂Cl₂ decreases with increasing substrate temperature, but that by HCl increases reversely. The present results were obtained by the same method of IR direct spectroscopy as already reported (5, 6), except that the quartz tubular reactor was evacuated and SiH₂Cl₂ was injected into the reactor at the pressure of 270-670 Pa and the H₂ or Ar carrier gas was not used. The absorption peak at about 590 cm⁻¹ did not disappear in high evacuation and at low temperatures, so the peak was thought to come from the adsorbate deposited in the window of the reactor.

The decomposition of SiH₂Cl₂ is enhanced at high temperatures above about 1000°C. In the measurement of only fluorescent light, the peaks at 500, 560, 780, 850, and 880 cm⁻¹ were observed. As already reported in previous work (2, 5) the emission at 500 and 560 cm⁻¹ was attributed to SiCl₂. Therefore, the intensities of these two peaks were measured as a function of substrate temperature as shown in Fig. 7.



Fig. 6. IR adsorption spectrum of SiH₂Cl₂ at a reduced pressure of 670 Pa, obtained by *in situ* IR spectroscopy at four different temperatures of 700°, 800°, 1000°, and 1100°C.



Fig. 7. Temperature dependence of emission intensities of reactants at 560 and 500 cm⁻¹ generated from SiH₂Cl₂ at a pressure of 270 Pa.

SiCl₂ disappears at about 900°C, which suggests the dissociation of SiH_2Cl_2 in the form

$$SiH_2Cl_2 \rightarrow SiCl_2 + H_2$$
 [6]

At the substrate temperatures higher than 900°C

$$SiH_2Cl_2 \rightarrow Si + 2HCl$$
 [7]

or by the reaction in a very short lifetime of SiCl₂

$$SiH_2Cl_2 \rightarrow SiCl_2 + H_2 \rightarrow Si + 2HCl$$
 [8]

or

$$SiH_2Cl_2 \rightarrow SiCl_2 + H_2 \rightarrow Si + H_2 + Cl_2 \rightarrow Si + 2HCl$$
 [9]

n⁺(111) Tsub:1050 °C P_{SiH2}Cl₂:0.5 Torr, 15min.



Fig. 8. The grain-like crystal islands grown on the (111) surface by the preliminary experiment, in which SiH₂Cl₂ was injected continuously for 900s at a pressure of 67 Pa. The substrate temperature was 1050°C.

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Fig. 9. Photomicrograph of the Si surface after the growth by the preliminary experiment of so-called reduced pressure epitaxy (a) without photoirradiation and (b) with irradiation by a Hg lamp at a substrate temperature of 1050°C.

Then, MLE by SiH_2Cl_2 is suggested to be available at a temperature slightly lower than 900°C.

At the temperatures above 900°C, self-decomposition of the SiH₂Cl₂ into Si can be expected. Prior to the growth by MLE, a preliminary experiment using the conventional CVD method was carried out. A flat epitaxial layer was obtained at temperatures above 1075°C by the reduced pressure epitaxy in which SiH₂Cl₂ was continuously injected and the carrier gas such as hydrogen was not used; at the temperatures below 650°C, no epitaxial growth took place. The growth in the form of small grain-like crystal islands



Fig. 10. Growth rate on the (111) surface as a function of SiH_2Cl_2 pressure at $T_{sub} = 1100^{\circ}C$ by the preliminary experiment (reduced pressure epitaxy) in which SiH_2Cl_2 was continuously injected.



Fig. 11. SEM microphotographs of grown films by MLE on the Si (100) surfaces with mask patterns of Si_3N_4/SiO_2 . The top layers of the mask patterns are Si_3N_4 (a) is the as-grown surface and (b) is the surface when the mask patterns are removed after the growth.

started at 700°-800°C, and continued up to about 1050°C as shown in Fig. 8.

The effect of the ultraviolet light irradiation could be observed slightly as shown in Fig. 9; the density of the generated small islands decreases with the irradiation, which does not contradict the usual explanation of expected enhancement of the migration of adsorbed species on the surface.

There, at the high temperature of 1100° C the dependence of growth rate on the SiH₂Cl₂ pressure is shown in Fig. 10, and if the pressure was lower than 130 Pa, the flat selective epitaxial layer growth was obtained on the window part of





Si Substrate

Fig. 12. SEM microphotographs of the selective epitaxial film by MLE at $T_{sub}=850^\circ C$ on the Si (100) surface with mask pattern of SiO_2.

the silicon substrate covered by the double layered mask pattern of silicon dioxide and silicon nitride, on which polycrystalline silicon deposited. On the basis of the above



Fig. 13. Time dependence of m/e = 36 intensities at the substrate temperatures of 850°, 750°, 650°, and 200°C in the case of the gas injection and the evacuation time mode of (40″, 3″, 10″, 7″).



Fig. 14. Time dependences of the intensities of m/e = 35 in the mass spectrum.



results of the preliminary experiment, the MLE growth by the alternative injection of SiH₂Cl₂ and H₂ was attempted. Some of these results of MLE growth are shown in Fig. 3-5. As shown in Fig. 11, the polycrystalline silicon deposited on the mask of silicon nitride and the edge of the grown silicon on the window edge next to the mask seems to be suppressed. And similar results are obtained in the selective growth by the silicon dioxide mask without silicon nitride as shown in Fig. 12. On the surface of silicon dioxide, there is no deposition of polycrystalline silicon, but the silicon surface shows lower flatness than in the case with silicon nitride. No silicon intermediate migrating species are deposited on silicon dioxide, and few adsorbed species on the silicon dioxide migrate out on the silicon epitaxial film. Hence, the growth thickness on the edge of the grown film next to the silicon dioxide mask is thin.

In the experiment of the cyclic injections of SiH₂Cl₂ followed by H₂, a Q mass spectrometer was used. Figures 13, 14 and 15 show the results of the measurements at m/e = 36, 35, and 28 intensity, respectively. In other m/e intensities at m/e = 100, 99, 98, and 63, 2, and 1, any response as the injection of hydrogen occurred could not be observed. It is quite probable that SiH₂Cl₂ decomposes into H₂ at the injection of SiH₂Cl₂ and some adsorbate decomposes into HCl and slight amounts of Cl and Si due to the reaction with H₂ at the injection of H₂; therefore, SiCl₂ seems to be a most promising adsorbate. Figures 16 and 17 show the generation of H₂ and H when SiH₂Cl₂ is injected and the comparison between the two figures strongly suggests the



Fig. 16. Transient responses of the intensities of m/e = 2 to the SiH₂Cl₂ injection onto the Si (100) surface.



Fig. 17. Transient responses of the intensities of m/e = 1

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Fig. 18. Transient responses of m/e = 36 intensities at the substrate temperatures of 700°, 750°, 800°, and 850°C.

possibility that the hydrogen atom is dissolved at first and combines with another hydrogen atom to form a hydrogen molecule

$$SiH_2Cl_2 \rightarrow SiCl_2 + 2H \rightarrow SiCl_2 + H_2$$
 [10]

For the precise measurement of the decomposition of HCl, the results as shown in Fig. 18 were measured. At the beginning, hydrogen was injected and the transient response of the m/e = 36 intensity was measured repeatedly, and the response corresponding to the release of HCl denoted as $S_1(t)$ was high in reproducibility. Considering the fact that the epitaxial growth of silicon could not be observed when the evacuation for more than 30s after the injection of SiH₂Cl₂, the quantity $S_1(t)$ or the release of m/e = 36 when hydrogen was injected should come from the adsorbate on the wall of the vessel and not from the substrate. Now, the quantities $S_0(t)$ and $B_0(t)$ are defined by

1. $S_0(t)$: the transient response of m/e = 36 intensity when hydrogen gas was injected after the injection of SiH₂Cl₂ was ceased following the gas injection and evacuation time mode of MLE growth.

2. $B_0(t)$: the transient response of m/e = 36 intensity in the mass spectrum of the residual gas without the injection of H₂ after the injection of SiH₂Cl₂ was ceased. This corresponds to the background quantity. The timing of the H₂ injection after the injection of SiH₂Cl₂ was shifted as denoted by a, b, and c in Fig. 18, and S₁(t) is substracted from the quantity S₀(t), with the background quantity B₀(t). Figure 19 shows the results of this subtraction $X(t) = S_0(t) - S_1(t) - B_0(t)$ as a function of the substrate temperature, which shows good coincidence with the lowest temperature of 775°C where the growth by MLE was







Fig. 20. Desorption spectrum of adsorbate on the Si (100) substrate as a function of substrate temperature after SiH₂Cl₂ injection at $T_{sub} = 200^{\circ}$ C. The substrate is heated gradually at a rate of 1 deg/s from 200° to 900°C.

observed; the significant amount of X(t)s is obtained at the substrate temperatures of 800° and 850°C and X(t)s are negligibly small below 750°C. That is, X(t)s above 800°C are ascribable to the released HCl by the reaction of injected H₂ and adsorbate on the surface of the substrate. Hence, SiCl₂ is suggested to be the adsorbate.

Figure 20 shows the release of dissolved molecules with the temperature rise after the injection of SiH_2Cl_2 at 200°C. The multilayer adsorbate evaporates at about 350°C with some $SiCl_2$ and is reduced into a single molecular layer. At about 450°C hydrogen was emitted, suggesting that a large amount of adsorbed SiH_2Cl_2 changes into $SiCl_2$, and at about 600°C HCl starts emitting.

Although, the above discussion revealed the reaction mechanism on the surface, autodoping of the boron profile by SIMS is shown in Fig. 21. The solid line labeled α_1 represents the profile of the 700Å thick epitaxial layer grown by mode A (20", 3", 5", 7") at 825°C. In Fig. 21, the dashed line α_2 represents the boron profile in the 900Å silicon layer grown at 825°C by mode A. Both cases show extremely high autodopings. The dashed lines (α_3 and α_4) represents the 1200 and 2000Å growth by SiH₂Cl₂ injection only. Although the differences between the growth time durations



Fig. 21. Autodoping profile of boron in the grown film. The solid line labeled α_1 represents the profile of the growth of 700Å thickness and the dashed line α_2 represents 900Å thickness by mode A. The dashed line α_3 represents the 1200Å growth, and the dashed line α_4 represents the 2000Å growth by only SiH₂Cl₂ injection (20", 7") without H₂.

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Fig. 22. Distribution profile of impurities in the grown film shown in Fig. 21 measured by SIMS.

seem very small, there is a distinct difference between the results of mode A growth and the growth without H₂ injection. The autodoping of boron is slightly lower in the case of SiH₂Cl₂ injection without hydrogen than the case with hydrogen (mode A). This phenomenon may be correlated with the large amount of backetch which seems to generate SiCl₂ or SiCl₃ as a result of HCl generation in the H₂ injection cycle rather than Cl₂ generation and the condensation on the wall of the vessel. The cooling of the vessel seems effective in reducing the contamination. However, further research must be made because the effect of the vessel wall on the QMS measurement is considered to be large.

In Fig. 22 the contaminations of carbon, oxygen, hydrogen, and chlorine measured by SIMS are increasing toward the surface. But the results about boron and other impurities do not coincide with each other. The process of gradual release of the many gases occluded in the grown film near the surface must be taken into account.

Conclusion

Using Q mass-spectroscopy, the surface adsorbate in the case of molecular layer epitaxial growth has been assumed to be mainly SiCl₂, which migrates on the silicon surface. However, the structure of the monomolecular layer is not so simple that there is great necessity to determine the variation in growth rate and mass spectrum with crystal orientation. Decomposition of hydrogen chloride at about 600° and 1000°C in Fig. 20 could not be explained, because the decomposed hydrogen had already been evacuated. There also remains the possibility of the adsorption on the surface of the substrate or on the adlayer in the form of SiH₂Cl₂ or SiHCl₂ which may decompose and release in small quantities.

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Activation of Be-Implanted GaAs by Using RTA with Proximity Contact

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ABSTRACT

Rapid thermal annealing (RTA) combined with proximity contact techniques has been used to activate Be-implanted GaAs. At the optimum RTA condition, which is 900°C for 5s, complete activation was achieved. The SIMS analyses show less dopant redistribution during RTA in comparison with furnace annealing. The proximity contact effectively suppressed arsenic loss and minimized GaAs surface morphology degradation.

Beryllium implantation is widely employed to form p-type layers in GaAs substrates. It achieves more versatile implant depths with less damage and good activation because Be has a very light mass. After implantation, hightemperature annealing is required for implant activation, and recovery from lattice damage. For GaAs, the annealing temperature range is above the congruent evaporation point (657° \pm 10°C), and this results in serious As loss and thermal erosion of the GaAs surface (1). In conventional furnace annealing, the GaAs surface has to be covered with a thin film of dielectric encapsulant, or annealed under stringent control of As overpressure. The use of dielectric film, however, can result in undesirable effects, such as stress-induced dopant diffusion (2), and interdiffusion between the encapsulant film and the GaAs substrate (3). Another problem associated with furnace annealing is dopant redistribution. This is a very difficult problem when dealing with fast diffusing p-type dopant, such as zinc. For Be-implanted samples annealed above 800°C, extremely rapid diffusion has been observed which gives rise to large dopant profile broadening (4).

Rapid thermal annealing has been successfully used to activate implanted dopants in semi-insulating GaAs (5-8). RTA has many advantages over furnace annealing. The short heating times make capless annealing possible, thus simplifying device processing and eliminating the stress-

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