

Acknowledgment

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Growth and Etching of Germanium Films by Chemical Vapor Deposition in a $\text{GeCl}_4\text{-H}_2$ Gas System

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ABSTRACT

The etching and growth of germanium films are investigated using a $\text{GeCl}_4\text{-H}_2$ gas system in the temperature range of 490°-565°C. At relatively low GeCl_4 partial pressures less than 2×10^{-3} torr, epitaxial growth of Ge is observed on Ge (100) surfaces, whereas at GeCl_4 partial pressures higher than 2×10^{-3} torr, etching of the Ge film is found to occur. In the experiments utilizing patterned substrates, where the surface consists of defined areas of Ge and SiO_2 , Ge is found to deposit selectively only on the exposed Ge regions. The growth reactions of Ge epitaxial films proceed through the Langmuir-Hinshelwood mechanism: the surface reaction takes place between two hydrogen atoms dissociatively adsorbed and a surface-adsorbed GeCl_2 molecule. GeCl_2 molecules adsorbed on the surface are formed directly from GeCl_4 molecules, not through gas-phase reduction by hydrogen. On the other hand, the etching reaction of Ge films is proved to be a reverse disproportionation reaction: $\text{GeCl}_4 + \text{Ge} \rightarrow 2\text{GeCl}_2$. Based on the analyses of growth and etching reactions, the equation of the Ge epitaxial film's growth rate is derived as a function of GeCl_4 partial pressure, hydrogen partial pressure, and growth temperature.

Recently, major interest has been shown in the application of Ge epitaxial film as an interlayer between a GaAs layer and a Si substrate (1, 2) or an ohmic contact layer in GaAs FET's (3). Chemical vapor deposition (CVD) and molecular beam epitaxy (MBE) have been used in order to form Ge epitaxial films. Compared with the MBE technique, one advantage of the CVD method is that ultrahigh vacuum cleaning of the substrate surface is unnecessary before Ge growth. Furthermore, another advantage of CVD is that selective growth applied for self-aligned LSI processes is possible since its film growth mechanism is based on surface chemical reactions (3, 10). For these reasons, the thermal decomposition of GeH_4 has been extensively studied (4-10). The crystalline quality and electrical properties of grown Ge films have been investigated and the growth mechanism has been clarified (10). Compared with GeH_4 system, the $\text{GeCl}_4\text{-H}_2$ gas system has not been examined in great detail. Cave *et al.* tried to apply Ge epitaxial films formed using this gas system for semiconductor device processes (11). Miller *et al.* reported that both growth and etching reactions of Ge film in the gas system occur depending on GeCl_4/H_2 mole ratio at a constant temperature of 880°C (12). However, the Ge film for-

mation mechanisms necessary to improve crystalline quality and thickness controllability have not yet been clarified.

The film growth mechanism in halide-hydrogen gas system of $\text{SiCl}_4\text{-H}_2$ was offered assuming chemical equilibrium in the gas phase (13). This assumption, however, is not reasonable since actual film growth conditions in CVD is in a nonequilibrium state (12). Analyses based on surface chemical reactions have successfully explained the film growth mechanisms in thermal decomposition of SiH_4 (14) and GeH_4 (10). The purposes of this work are, from the viewpoint of surface chemical reaction, to clarify the Ge epitaxial film growth and etching mechanisms in a $\text{GeCl}_4\text{-H}_2$ gas system and to derive the equation of the Ge epitaxial film growth rate as a function of GeCl_4 partial pressure, hydrogen partial pressure, and growth temperature.

Experimental

A low pressure CVD apparatus with a lamp-heated horizontal reactor was used. The experiments were performed in the temperature range of 490°-565°C under a total pressure of 6.5 torr. The temperature was monitored by an optical pyrometer and the pressure was measured with a ca-

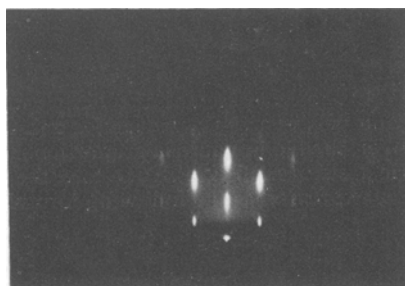


Fig. 1. Electron diffraction pattern for Ge film grown at 540°C for P_{GeCl_4} of 9.0×10^{-4} torr in a $\text{GeCl}_4\text{-H}_2$ gas system.

pacitance manometer. A $\text{GeCl}_4\text{-He}$ gas system was used to study the GeCl_4 partial pressure P_{GeCl_4} dependence of the etching rate, P_{GeCl_4} was varied from 9.0×10^{-4} to 1.3×10^{-2} torr. In addition, a $\text{GeCl}_4\text{-H}_2\text{-He}$ gas system was used to investigate hydrogen partial pressure P_{H_2} dependence of etching and growth rates, in which P_{H_2} was varied between 0 and 6.5 torr. The role of helium gas introduced was to maintain the total pressure of 6.5 torr as the P_{H_2} was varied. The substrates used here were Ge (100) films formed on Si (100) wafers by CVD using a $\text{GeH}_4\text{-H}_2$ gas system (10). The Ge (100) film thickness was 500Å and 2000Å for the growth and etching experiments, respectively. The Ge film thickness was measured by a Talystep. Element analysis on the prepared sample surfaces was performed with Auger electron spectroscopy (AES). The structure of grown Ge films was checked using electron diffraction.

Results

A typical diffraction pattern of Ge film grown using a $\text{GeCl}_4\text{-H}_2$ gas system is shown in Fig. 1. From the figure, Ge is found to grow epitaxially on a Ge (100) surface. Moreover, the epitaxial Ge films were obtained only on Ge (100) substrate surfaces. No Ge deposition was found on SiO_2 surfaces. This was confirmed by AES. The Ge selective epitaxial growth was observed for all deposition conditions employed in the experiments. An example of the Ge selective growth is shown in Fig. 2. The light and dark sections of the wafer indicate Ge film grown selectively on a Ge (100) surface and nondeposited SiO_2 surface, respectively.

Figure 3 shows P_{GeCl_4} dependence of growth rates and the temperature parameters in the $\text{GeCl}_4\text{-H}_2$ gas system. It was found that the growth rates increase to a maximum and then decrease to minus values as P_{GeCl_4} increases. In addition, the growth rate at each temperature seems to have its asymptote. Minus growth rate values will be referred to as etching rates throughout this paper. Figure 4 shows P_{GeCl_4} dependence of growth rates at 540°C using a

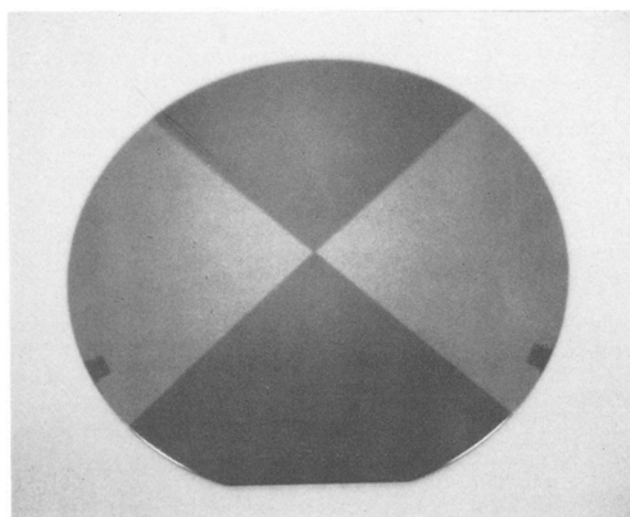


Fig. 2. Ge selective growth at 540°C for P_{GeCl_4} of 9.0×10^{-4} torr in a $\text{GeCl}_4\text{-H}_2$ gas system. Light and dark areas show selectively grown Ge and SiO_2 ones, respectively.

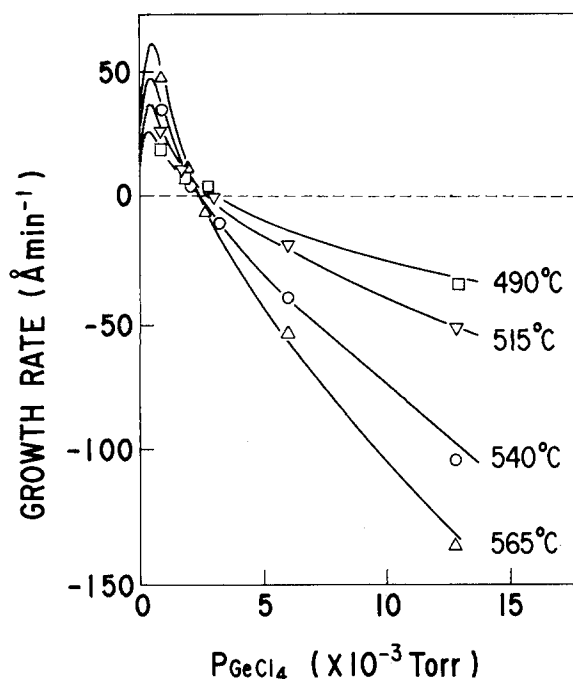


Fig. 3. GeCl_4 partial pressure dependence of growth rate in a $\text{GeCl}_4\text{-H}_2$ gas system. The solid curves were obtained from Eq. [11] by curve-fitting.

$\text{GeCl}_4\text{-He}$ gas system where helium gas takes the place of H_2 in the $\text{GeCl}_4\text{-H}_2$ gas system. In the $\text{GeCl}_4\text{-He}$ gas system, no Ge growth is observed and etching alone takes place in any P_{GeCl_4} . This clearly indicates that hydrogen is necessary for the Ge film growth. Furthermore, the etching rate is found to be proportional to P_{GeCl_4} . The solid line of Fig. 4 seems to correspond to the asymptote referred to earlier. On the other hand, both the growth rates at P_{GeCl_4} of 9.0×10^{-4} torr in the $\text{GeCl}_4\text{-H}_2$ gas system and the etching rates in the $\text{GeCl}_4\text{-He}$ system showed no change when the gas-flow velocity in the CVD reactor was diminished to 67% by reducing the conductance of the evacuation system. The independence of growth and etching rates from the gas-flow velocity shows that the growth and etching reactions are controlled by surface chemical reactions, not by the

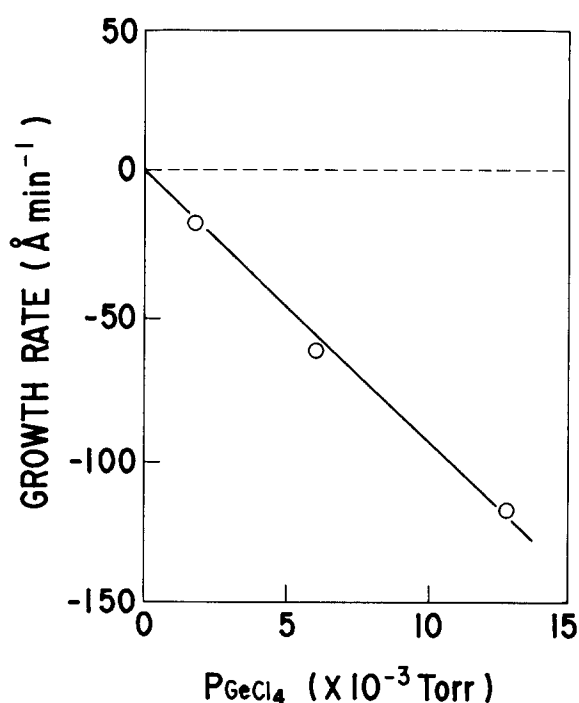


Fig. 4. GeCl_4 partial pressure dependence of growth rate in a $\text{GeCl}_4\text{-He}$ gas system at 540°C.

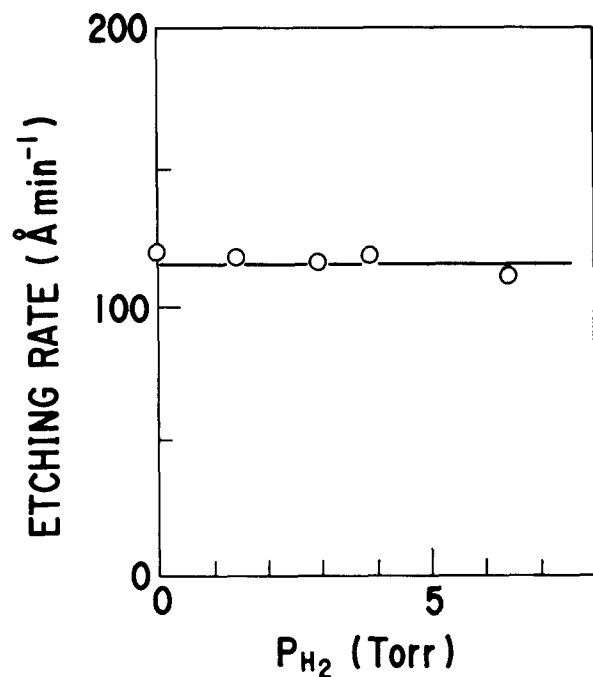


Fig. 5. Hydrogen partial pressure dependence of etching rate in a $\text{GeCl}_4\text{-H}_2\text{-He}$ gas system at 540°C for P_{GeCl_4} of 1.3×10^{-2} torr.

diffusion of GeCl_4 . To make clear the influence of hydrogen on the etching and growth reactions, the dependence of P_{H_2} on etching and growth rates was investigated using the $\text{GeCl}_4\text{-H}_2$ gas system. The results are shown in Fig. 5 and 6. Figure 5 shows the dependence of P_{H_2} on the etching rates at 540°C for P_{GeCl_4} of 1.3×10^{-2} torr. From the figure, it can be seen that the etching rates are almost constant. This indicates that the etching reaction is independent of hydrogen. Figure 6 shows P_{H_2} dependence of the growth rates at 540°C for P_{GeCl_4} of 9.0×10^{-4} torr. This figure indicates the linear relationship between P_{H_2} and the growth rates.

Discussion

Film etching reaction process.—As shown in Fig. 4, only etching reaction occurs in the $\text{GeCl}_4\text{-He}$ gas system. The etching rate in the $\text{GeCl}_4\text{-H}_2$ gas system is nearly equal to that in the $\text{GeCl}_4\text{-He}$ gas system at 540°C and a P_{GeCl_4} higher than 6.0×10^{-3} torr. This means that the etching reaction in the $\text{GeCl}_4\text{-H}_2$ gas system at a P_{GeCl_4} higher than 6.0

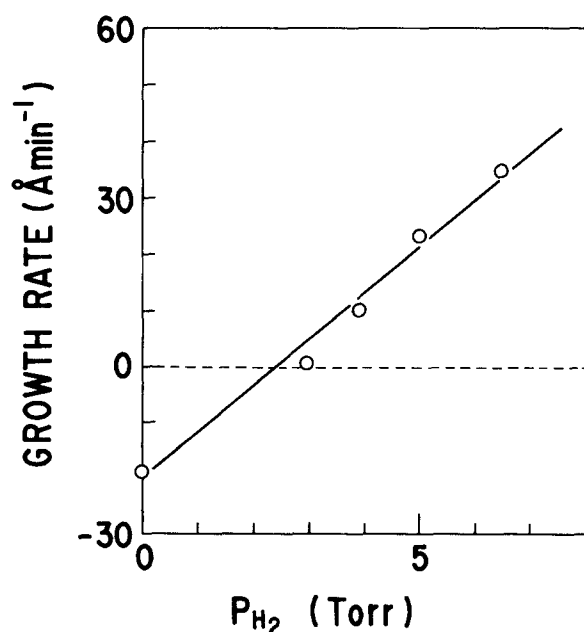
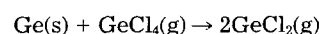


Fig. 6. Hydrogen partial pressure dependence of growth rate in a $\text{GeCl}_4\text{-H}_2\text{-He}$ gas system at 540°C for P_{GeCl_4} of 9.0×10^{-4} torr.

$\times 10^{-3}$ torr takes place unrelated to hydrogen. The etching rate is, actually, independent of P_{H_2} , as shown in Fig. 5. This independence of the etching reaction from hydrogen apparently indicates that etching is mainly caused by the direct reaction between GeCl_4 molecules and the Ge surface. Moreover, the etching rate is proportional to P_{GeCl_4} in the $\text{GeCl}_4\text{-He}$ gas system (Fig. 4). Therefore, the etching reaction can be expressed as the following formula



where (s) and (g) stand for the solid state and gas phase, respectively. This reaction is a reverse disproportionation reaction. This conclusion is supported by the fact that germynes — *i.e.*, divalent germanium derivatives — are fairly stable in a $\text{Ge-GeCl}_2\text{-GeCl}_4$ system (15, 16). The etching rate R_E is given by

$$R_E = k_E \times P_{\text{GeCl}_4} \quad [1]$$

where k_E is the reaction rate constant. Figure 7 shows temperature dependence of the etching rate at P_{GeCl_4} of 1.3×10^{-2} torr. Using the results of the figure, the value of k_E is given as

$$k_E = 2.2 \times 10^{10} \times \exp(-1.04 \text{ eV}/kT) \text{ Å min}^{-1} \text{ torr}^{-1}$$

where k and T are Boltzmann constant and absolute temperature, respectively. The high activation energy of 1.04 eV suggests that the etching reaction is controlled by the surface chemical reaction rather than the diffusion of GeCl_4 . This is consistent with the fact that the etching rate is independent of the gas-flow velocity in the CVD reactor.

Film growth reaction mechanism.—As was explained above, the etching reaction takes place between GeCl_4 molecules and solid Ge. Therefore, growth rate R_G shown in Fig. 3 includes the contribution from the etching reaction in addition to the growth reaction. As is pointed out above in the Results section, each curve for P_{GeCl_4} dependence of growth rate R_G has a steep rise to a peak, which then gradually falls off to approximate to its asymptote. This asymptote corresponds to R_E as expressed in Eq. [1], because the values of R_G and R_E almost agree in the high P_{GeCl_4} region. Thus, the net growth rate R_{Gn} can be approximately obtained by the following equation

$$R_{Gn} = R_G + R_E \quad [2]$$

In order to distinguish the growth reaction characteristics

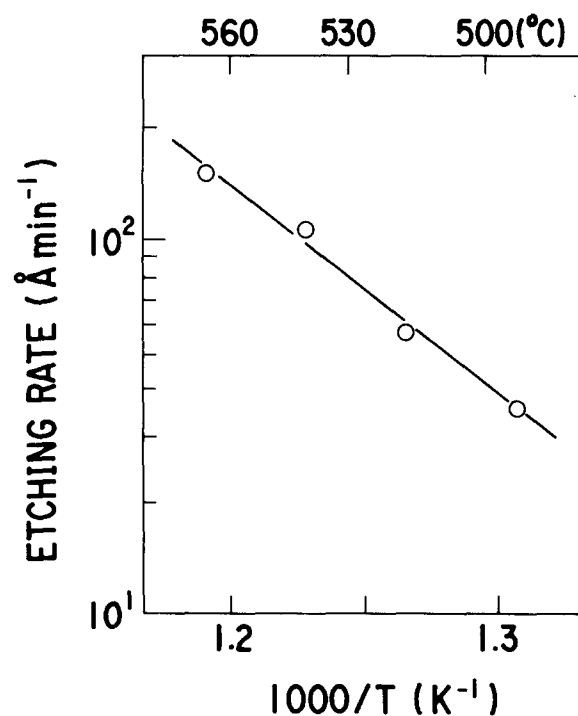


Fig. 7. Temperature dependence of etching rate at P_{GeCl_4} of 1.3×10^{-2} torr in a $\text{GeCl}_4\text{-H}_2$ gas system.

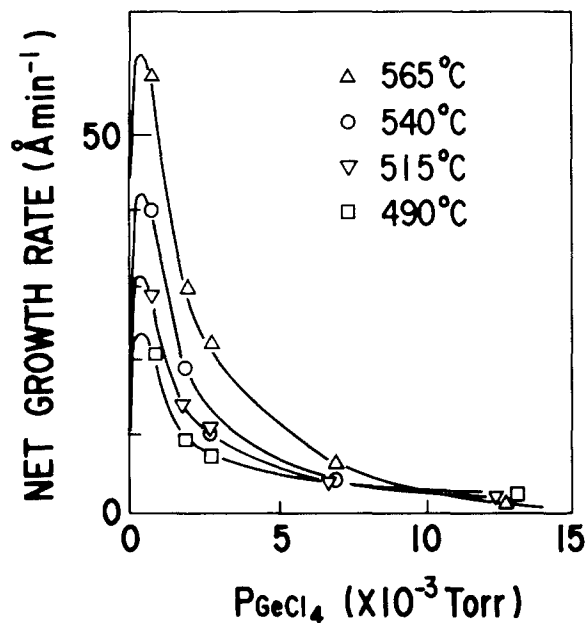
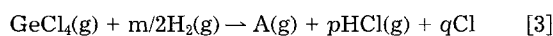


Fig. 8. GeCl_4 partial pressure dependence of net growth rate R_{Gn} given by Eq. [2].

from the etching reaction ones, P_{GeCl_4} dependence of net growth rate R_{Gn} is shown in Fig. 8 by incorporating the R_G data shown in Fig. 3 and the R_E values given by Eq. [1]. Here too, each curve for R_{Gn} has a steep rise to a maximum, followed by a steep fall as P_{GeCl_4} increases. From the chemical viewpoint, this is characteristic of the Langmuir-Hinshelwood (L-H) mechanism. Namely, Ge epitaxial film growth reaction using a $\text{GeCl}_4\text{-H}_2$ gas system proceeds via the surface reaction between a Ge compound adsorbate derived from GeCl_4 and hydrogen atoms adsorbed on the surface. Therefore, the growth reaction processes can tentatively be written as follows



A, derivative from GeCl_4 ; (g), gas phase; (ads), adsorption state; (s), solid state; m , n , p , q , and r , 0 or natural number where reaction [3] represents the formation reaction of A and reactions [4] and [5] show the equilibrium reaction of A and hydrogen between their adsorption state and gas phase, respectively. Reaction [6] is the surface reaction of the adsorbates to form solid Ge.

Formulation of the growth rate.—In the following discussion, growth rate R_G is formulated as a function of P_{GeCl_4} , P_{H_2} , and T . Let surface coverage of A and hydrogen atom be θ_A and θ_H , respectively. θ_A and θ_H are expressed according to Langmuir's adsorption isotherm as

$$\theta_A = \frac{\alpha P_A}{1 + \alpha P_A + \beta P_{\text{H}_2}^{1/2}}$$

$$\theta_H = \frac{\beta P_{\text{H}_2}^{1/2}}{1 + \alpha P_A + \beta P_{\text{H}_2}^{1/2}}$$

in which α and β are the equilibrium constant for the adsorption in reactions [4] and [5], respectively, and P_A is the partial pressure of A. From reaction [6], R_{Gn} is written as

$$R_{Gn} = k_{Gn} \times \theta_A \times \theta_H^n$$

$$= \frac{k_{Gn} \times \alpha \beta^n \times P_A \times P_{\text{H}_2}^{n/2}}{(1 + \alpha P_A + \beta P_{\text{H}_2}^{1/2})^{(n+1)/2}} \quad [7]$$

where k_{Gn} is the reaction rate constant in reaction [6]. From reaction [3], P_A is given as

$$P_A = \gamma \times P_{\text{GeCl}_4} \times P_{\text{H}_2}^{m/2}$$

where γ is the reaction rate constant in reaction [3]. Substituting $\gamma \times P_{\text{GeCl}_4} \times P_{\text{H}_2}^{m/2}$ for P_A in Eq. [7], R_{Gn} is obtained by

$$R_{Gn} = \frac{k_{Gn} \times \alpha \beta^n \times P_{\text{GeCl}_4} \times P_{\text{H}_2}^{(m+n)/2}}{(1 + \alpha \gamma \times P_{\text{GeCl}_4} \times P_{\text{H}_2}^{m/2} + \beta P_{\text{H}_2}^{1/2})^{(n+1)/2}} \quad [8]$$

On the other hand, since the relationship of R_G to P_{H_2} is a linear one (Fig. 6), R_{Gn} is expressed as

$$R_{Gn} = \frac{k_G \times P_{\text{GeCl}_4} \times P_{\text{H}_2}^{(m+n)/2}}{(1 + k_{\text{ads}} \times P_{\text{GeCl}_4} \times P_{\text{H}_2}^{m/2} + k^* \times P_{\text{H}_2}^{1/2})^{(n+1)/2}} \quad [9a]$$

$$= f(P_{\text{GeCl}_4}) \times P_{\text{H}_2} \quad [9b]$$

in which $k_{Gn} \alpha \beta^n \gamma$, $\alpha \gamma$, and β in Eq. [8] are rewritten as k_G , k_{ads} , and k^* , respectively, and $f(P_{\text{GeCl}_4})$ shows the function of P_{GeCl_4} . Equation [9b] using P_{GeCl_4} , which is identical to Eq. [9a], is satisfied only when $k^* = 0$, $m = 0$, and $n = 2$. Therefore, R_{Gn} is obtained by

$$R_{Gn} = \frac{k_G \times P_{\text{GeCl}_4} \times P_{\text{H}_2}}{(1 + k_{\text{ads}} \times P_{\text{GeCl}_4})^3} \quad [10]$$

Using the relation given by Eq. [2], growth rate R_G can be expressed as

$$R_G = \frac{k_G \times P_{\text{GeCl}_4} \times P_{\text{H}_2}}{(1 + k_{\text{ads}} \times P_{\text{GeCl}_4})^3} - k_E \times P_{\text{GeCl}_4} \quad [11]$$

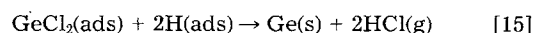
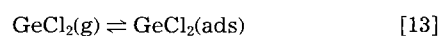
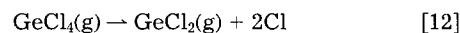
By curve-fitting method, unknown parameters k_G and k_{ads} in Eq. [11] are determined as

$$k_G = 1.5 \times 10^8 \times \exp(-0.544 \text{ eV}/kT) \text{ Å min}^{-1} \text{ torr}^{-1}$$

$$k_{\text{ads}} = 2.8 \times 10^2 \times \exp(0.100 \text{ eV}/kT) \text{ torr}^{-1}$$

The solid curves in Fig. 3 show the result of the curve fitting. It can be seen that the calculated and experimental growth rate values are closely approximated. This suggests that reactions [3]-[6] based on the L-H mechanism are valid for Ge growth in a $\text{GeCl}_4\text{-H}_2$ gas system. In the procedure for obtaining Eq. [11], k^* is given as 0. This is equivalent to the fact that hydrogen-adsorption term $\beta P_{\text{H}_2}^{1/2}$ in Eq. [8] can be omitted. Its chemical significance is that hydrogen molecules are hard to adsorb dissociatively on the Ge surface (17) compared with GeCl_4 derivative, A. Actually, the partial pressure of hydrogen which is necessary to grow Ge epitaxial film is higher than that of GeCl_4 by a factor of 2000-7000. This is ascribed to the difficulty of dissociative adsorption for hydrogen molecules on the surface.

Film growth reaction process.—In this section, film growth reaction processes are proposed based on the values of m and n obtained as 0 and 2 in the earlier discussion. The result, $n = 2$, shows that two hydrogen atoms which are dissociatively adsorbed react with A on the surface in reaction [6] and also shows that A is in the form of GeCl_2 stoichiometrically. Furthermore, the fact that $m = 0$ suggests that the adsorbate, GeCl_2 in reaction [3] is formed directly from GeCl_4 without reduction by hydrogen in the gas phase. Therefore, the possible reaction processes are given as



In reaction [12], gaseous GeCl_2 is expressed as the decom-

position product of gaseous GeCl_4 . This reaction hardly occurs, however, because GeCl_4 molecules are quite stable in the gas phase. Therefore, the decomposition of GeCl_4 via heterogeneous catalytic reaction between GeCl_4 and a surface may take place as is reported for Si epitaxy in a $\text{SiCl}_4\text{-H}_2$ gas system (18). Detailed verification of reaction [12] must be investigated further.

Conclusion

Growth and etching reactions of Ge epitaxial films in a $\text{GeCl}_4\text{-H}_2$ gas system are investigated at temperatures between 490° and 565°C. In this temperature range, the Ge films grow only on Ge (100) surfaces, but not on SiO_2 surfaces. The Ge film etching reaction is proved to be the reverse disproportionation reaction: $\text{GeCl}_4 + \text{Ge} \rightarrow 2\text{GeCl}_2$. The film growth reaction is found to take place via the Langmuir-Hinshelwood mechanism: a surface-adsorbed GeCl_2 molecule derived directly from GeCl_4 without reduction by hydrogen in the gas phase reacts with two surface-adsorbed hydrogen atoms on the surface. In addition, Ge epitaxial film growth reaction processes are proposed. Based on analyses, the film growth rate is formulated as a function of GeCl_4 partial pressure, hydrogen partial pressure, and growth temperature.

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Characterization of Enhanced Barrier Schottky Diodes Impurity Profiling in the Punch-Through Region

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ABSTRACT

We have established a theoretical basis for impurity profiling of the punch-through p-layer in metal-p⁺-n structures and have successfully applied this to Au/n-GaAs enhanced barrier diodes having a shallow Be implant under the metal. The theory uses the thermionic emission model for electron conduction over the barrier. Use of our model to interpret Schottky diode current-voltage characteristics and capacitance-voltage data yields the spatial dependence of the activated Be implant. Normal capacitance-voltage analysis can profile only part of the n-region and not the p-region in punch-through. Our results scale with the SIMS profile of the annealed 5 keV Be implant. This analytical profiling approach can be extended to any one-dimensional system in punch-through. In applying our model to the enhanced barrier Schottky diodes investigated here, we found that the model was indeed very general; the availability of unimplanted control Schottky diodes enabled us to show that we could extend the region of analysis beyond the usual linear range of the logarithm of current vs. voltage to a very high current range in which series resistance is often erroneously thought to be a limiting effect.

Enhancement of Schottky barrier heights due to the introduction of a thin p⁺ region near the interface of a metal/n-type semiconductor Schottky junction was first demonstrated in the 1970's for CdS (1) and Si (2-4). More recently, enhanced barrier height Schottky junctions have been receiving increased attention with respect to III-V semicon-

ductors. A number of applications have prompted this including: enhancement mode GaAs MESFET's with improved noise margin and relaxed tolerance on threshold voltage uniformity (5); high speed MESFET's using GaInAs (6); and a MESFET technology for InP (7). Accordingly, since these p⁺ doping effects occur very near the metal-semiconductor interface, it is very desirable to develop analytical techniques for characterization of the degree of ionization and spatial dependence of the doping in

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