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LOW-TEMPERATURE SILICON AND GERMANIUM CVD IN ULTRACLEAN ENVIRONMENT

J. MUROTA, M. KATO, R. KIRCHER⁽¹⁾ and S. ONO

*Laboratory for Microelectronics, Research Institute of
Electrical Communication, Tohoku University, 2-1-1 Katahira,
Aoba-ku, Sendai 980, Japan*

Abstract.—Low-temperature Si and Ge CVD processing was investigated under the cleanest possible reaction environment of SiH_4 , GeH_4 and H_2 using an ultraclean hot-wall low-pressure CVD system. Epitaxial growth can be achieved on Si substrates at temperatures as low as 350 and 550°C for Ge and Si, respectively. The deposition rate can be expressed by an equation similar to the Langmuir adsorption isotherm as a function of SiH_4 and H_2 partial pressure for Si CVD, and only GeH_4 partial pressure for Ge CVD with excellent agreement. The substrate orientation dependence of the deposition rate shows that the surface reaction proceeds at adsorption sites composed of dangling bonds on the surface. It is found that the SiH_4 decomposition induces nucleation on Si oxide. The nucleation rate is suppressed by the presence of GeH_4 and decreases on CVD BPSG compared with SiO_2 . Therefore, by a proper choice of deposition temperature, SiH_4 and GeH_4 partial pressure, as well as of the insulating oxide, 500nm-thick selective growth of Si at 850°C and Si-Ge alloy at 550°C could be realized. A perfect selective growth of Ge between Si and SiO_2 is obtained. At low surface coverages of GeH_4 on Si, facets are formed due to a step-flow dominated growth mechanism. At high surface coverages, plane surfaces are obtained due to dangling bond dependent growth mechanisms.

1.—Introduction.

Low-temperature Si and Ge CVD processing is attractive for progress in future semiconductor devices, e.g. three-dimensional devices and hetero-devices, because of the ability to fabricate abrupt transitions in doping concentrations and tailor the bandgap of Ge/Si hetero-structures /1/. It also offers many advantages such as high throughput, selective deposition and in situ doping compared with other film formation methods. Generally, the quality of epitaxial films is degraded at lower epitaxial temperatures because more impurities are incorporated from the reaction environment at these temperatures. In order to perform high quality low-temperature epitaxial CVD, it is important to reduce contamination in CVD processing /2,3/. In the present work, low-temperature Si and Ge CVD processing was investigated under the cleanest possible reaction environment of SiH_4 , GeH_4 and H_2 using an ultraclean hot-wall low-pressure CVD system. Epitaxial growth has been realized on Si substrates at temperatures as low as 350 and 550°C for Ge and Si, respectively. In addition, we discuss several selective deposition mechanisms.

2.—Contamination-minimized CVD processing.

The ultraclean hot-wall low-pressure CVD system used in our experiments is schema-

⁽¹⁾ Siemens AG, Corp, Research and Development,
D-8000 Muenchen 83, Germany

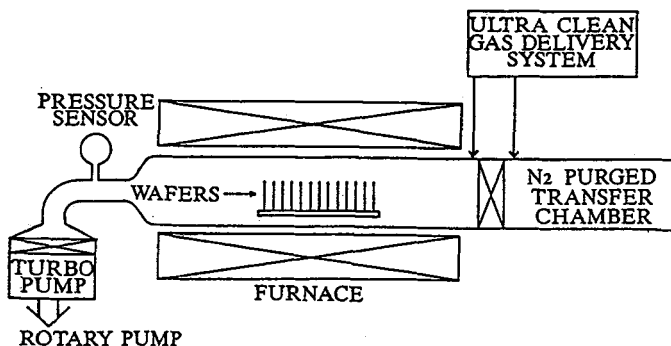


Fig.1.-Schematic diagram of an ultraclean hot-wall low-pressure CVD system.

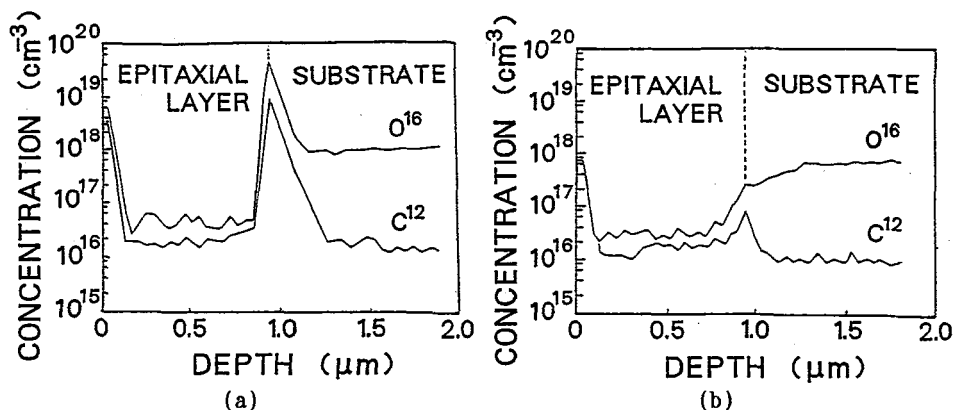


Fig.2.-The contamination by O and C during wafer loading into the reactor at reactor temperature of (a) 600°C and (b) about 100°C. The epilayer was deposited for 12 minutes with a 60 sccm SiH_4 gas flow and a 340 sccm H_2 gas flow at a temperature of 750°C and a total deposition pressure of 20 Pa. The depth-profiles of O and C in the deposited samples were evaluated by secondary ion mass spectrometry.

tically shown in Figure 1 /4,5/. The reactor structure is the same as that of a conventional hot-wall low-pressure CVD system /6/. An oil free turbo molecular pump system, which was improved to vacuum-evacuate from atmospheric pressure, was used in the deposition pressure region below 667 Pa. An ultimate vacuum level of about 10^{-6} Pa is reached in the reactor, i.e., the system is ultrahigh vacuum compatible. To minimize air-contamination in the reactor during the wafer load and unload, a N_2 purged transfer chamber was combined with the reactor inlet. The wafers, placed on a quartz boat, are transported into the reactor under ultraclean N_2 atmosphere through the transfer chamber. After closing the gate valve, the N_2 flow stops and the reactor tube is purged with high-purity H_2 . In order to prevent any contamination from the exhaust line, the purge gas is flowing permanently during vacuum pumping. Subsequently, high-purity reactive gas is added and the Si and/or Ge deposition starts. Here, the moisture level of the N_2 , H_2 and SiH_4 gases used was 10 ppb or lower and that of GeH_4 was 23 ppb or lower at the reactor inlet /7/. Before loading the wafers into the transfer chamber, they were cleaned in several cycles in a 4:1 solution of H_2SO_4 and H_2O_2 or in hot $\text{NH}_4\text{OH}-\text{H}_2\text{O}_2-\text{H}_2\text{O}$ and hot $\text{HCl}-\text{H}_2\text{O}_2-\text{H}_2\text{O}$ solutions, high-purity DI water, and 2% HF.

As illustrated in Figure 2, an impurity pile-up at the interface between epilayer

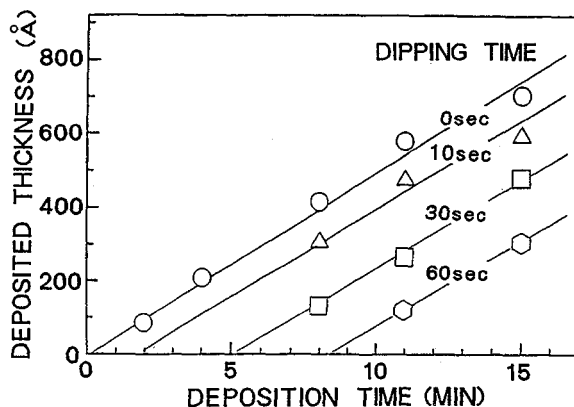


Fig.3-Deposition time dependence of deposited Ge thickness on Si(100) substrates at a GeH_4 partial pressure of 1.7 Pa and a deposition temperature of 400°C . Prior to deposition, the substrates were dipped in a H_2O_2 solution.

and Si substrate can be removed by a new process sequence, where wafers are transported into the reactor at a reactor temperature of about 100°C and then heated-up to deposition temperature while purging with H_2 gas under a pressure of about 200 Pa /8/. By this method, no pile-up of O and C at the interface is found above the background level. It is considered that, at temperatures between 100°C and the deposition temperature, impurities adsorbed on substrate surfaces before loading are desorbed /9/, and/or some reactions between the substrate surface and impurities diffusing from the exhaust line during the wafer loading are suppressed by decreasing reactor temperature. It was found that the native oxide on the Si surface was reduced by ultrapure SiH_4 and GeH_4 . Even for Si deposition at 650°C on the native oxide formed in a hot $\text{NH}_4\text{OH}-\text{H}_2\text{O}_2-\text{H}_2\text{O}$ solution, Si epitaxy was possible /4/. A typical example indicating the reduction of the native oxide on the Si surface by GeH_4 is shown in Figure 3. Here, the native oxide was formed by dipping the samples in a H_2O_2 solution. The dipping leads to a incubation period for Ge deposition, and the incubation period increases proportionally with the dipping time. Without dipping, almost no incubation period is observed. This result means that the native oxide is reduced by GeH_4 . Similar results for Si deposition can be obtained. It should be noted that the incubation period was not observed and epitaxial growth was realized at a deposition temperature above 350°C for Ge deposition, and above 550°C for Si deposition just after 2% HF dipping and 5 minute high-purity DI water rinse.

3.-Epitaxial growth mechanism.

It is considered that SiH_4 or GeH_4 is adsorbed at adsorption sites based on a Langmuir adsorption isotherm, and decomposes into Si or Ge at adsorption sites. Then, the deposition rate of Si or Ge is given by the following equation

$$R = k n_0 K_A P_A / (1 + K_A P_A + K_H P_{\text{H}_2}). \quad (1)$$

Here, k is the rate constant for the surface reaction of SiH_4 or GeH_4 , n_0 the adsorption site density at the surface, and K_A and K_H are the adsorption equilibrium constants, P_A and P_{H_2} the SiH_4 or GeH_4 and H_2 partial pressures, respectively. Equation (1) means that, for lower P_A such as $1 \gg K_A P_A$, the deposition rate increases proportionally with P_A , while for higher P_A such as $1 \ll K_A P_A$, the deposition rate is independent of P_A .

For Si deposition in the temperature range $550 - 650^\circ\text{C}$, the deposition rate is expressed by equation (1). The fitting parameters are weakly dependent on the

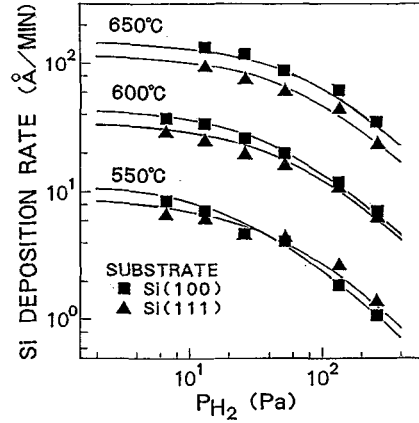


Fig.4.- H_2 partial pressure dependence of the Si deposition rate on Si(100) and Si(111) substrates for various deposition temperatures at a SiH_4 partial pressure of 1.3 Pa.

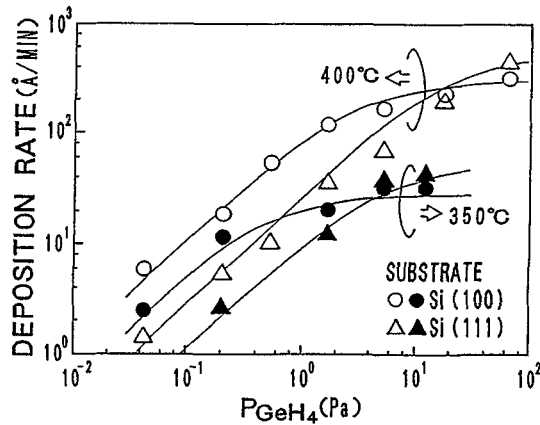


Fig.5.- GeH_4 partial pressure dependence of the Ge deposition rate for deposition temperatures of 350 and 400°C, on Si(100) and Si(111) substrates. The solid lines are the results obtained from the equations (1) - (5). H_2 is used as carrier gas.

substrate orientation, and the deposition rate is limited by the chemisorption of gaseous H_2 as shown in Figure 4 /10/. On the other hand, for Ge deposition in the temperature range 350 - 400°C, the fitting parameters are strongly dependent on the substrate orientation, and the chemisorption of H_2 molecules on the Ge surface can be neglected for H_2 partial pressures below 133 Pa /11/. The results (solid curves shown in Figure 5) obtained from equation (1) are in good agreement with the experimental data. For the deposition on Si(100), the following parameters have been used;

$$kn_{O(100)} = 6.9 \times 10^{14} \exp(-1.65\text{eV}/kT), \quad (\text{\AA}/\text{min}) \quad (2)$$

$$K_{A(100)} = 3.3 \times 10^{-10} \exp(1.2\text{eV}/kT), \quad (\text{Pa}^{-1}) \quad (3)$$

and for the deposition on Si(111),

$$kn_{O(111)} = 1.2 \times 10^{15} \exp(-1.65\text{eV}/kT), \quad (\text{\AA}/\text{min}) \quad (4)$$

$$K_{A(111)} = 5.5 \times 10^{-11} \exp(1.2\text{eV}/kT). \quad (\text{Pa}^{-1}) \quad (5)$$

The activation energy of GeH_4 decomposition, given by equations (2) and (4), is independent of the substrate orientation, and is in good agreement with that reported by Tamaru et al./12/ which is equal to the sum of the activation energy (0.63 eV) for hydrogen desorption and the heat (1.02 eV) of hydrogen adsorption. From the equations (1) - (5), it is clear that, for lower P_A , the surface coverage $KP_A/(1 + KP_A)$ of GeH_4 on a (100) surface is about 6 times larger than that on a (111) surface, and as a result, the deposition rate on (100) surface is higher than that on (111) surface. For higher P_{GeH_4} , the surface coverage is unity for (100) and (111) surfaces and kn_0 on (111) surface is 1.7 times larger than that on a (100) surface. Therefore, the deposition rate on (111) surfaces is higher than that on (100) ones. The values of K_A and kn_0 were calculated from the deposition data on various differently oriented substrates. For the (100) surface K_A has the largest value. Because the density of hollow bridge sites, which is composed of opposite dangling bonds from two surface atoms, is largest on the (100) surface, the hollow bridge sites are considered to play the role as the strongest adsorption sites /13/. On the other hand, the adsorption site density n_0 is considered to include not only the hollow bridge site density but also the other dangling bonds, because the value of kn_0 , normalized with respect to the (100) surface value, is nearly equal to the normalized number of available bonds, except for the (311) surface. Consequently, it is proposed that the surface reaction of GeH_4 proceeds at adsorption sites composed of dangling bonds on the surface /14/. The large difference in the sub-strate orientation dependence of kn_0 and K_A between Si and Ge deposition could mean that the role of dangling bonds as adsorption sites depends on the temperature as well as the deposited material.

For Si-Ge alloy deposition at the temperature 550 °C, the SiH_4 reaction rate increases up to a maximum value and then decreases with increasing GeH_4 partial pressure, as shown in Figure 6 /10/. This behavior is more pronounced on (100) surfaces than (111) ones. Since it has been found that the GeH_4 reaction rate increases monotonically with GeH_4 partial pressure, it is considered that Si-hydride adsorption is not inhibited by Ge-hydride adsorption. It was also found that the maximum SiH_4 reaction rate shown in Figure 6 was at the Ge concentration of 50% in the deposited films. Therefore, it is suggested that the adsorption equilibrium and/or reaction rate constants of SiH_4 have the maximum at hollow bridge sites which are composed of opposite dangling bonds from Si and Ge, whose density is larger on (100) surfaces compared with (111) ones.

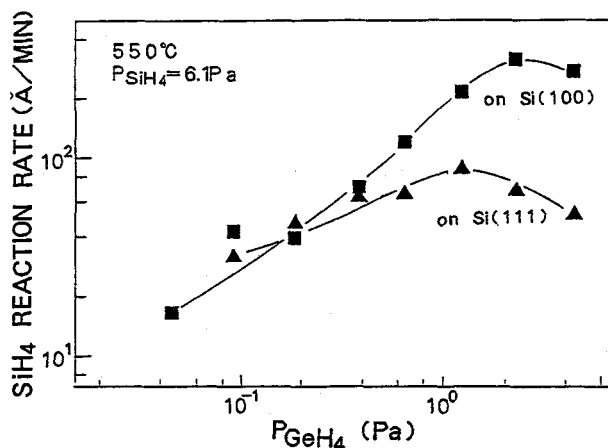


Fig.6.- GeH_4 partial pressure dependence of the SiH_4 reaction rate at a deposition temperature of 550°C, a total pressure of 27 Pa and a SiH_4 partial pressure of 6.1 Pa.

4.-Selective epitaxy.

By minimizing contamination in CVD processing, an incubation period for Si deposition on Si oxide has been found /4,5/. As a result, during this incubation period, Si is selectively deposited only on Si at low temperatures. The existence of the incubation period for oxide only means that the adsorption site density is negligibly small on the oxide surface, compared with that on the Si surface. In order to obtain high selectivity between Si and Si oxide, it is necessary to reduce the number of Si-hydride molecules or Si atoms adsorbed on the oxide surface. The incubation period is prolonged and Si nucleation rate is decreased on CVD phospho- or boro-silicate glass compared with thermal SiO₂. Based on these results, the selective Si epitaxy was realized in via-holes opened in CVD boro-phospho-silicate glass on Si(100) substrates at temperatures as low as 850°C /15/. With the addition of GeH₄ to SiH₄, a suppression of nucleation was found as shown in Figure 7. Since the deposition rate increases drastically with GeH₄ addition, selective Si-Ge epitaxy can be realized at lower temperatures compared with the selective Si epitaxy. Figure 8 shows Si-Ge fillings deposited at 550 °C in via-holes opened in CVD boro-phospho-silicate glass and CVD SiO₂ on Si(100) substrates.

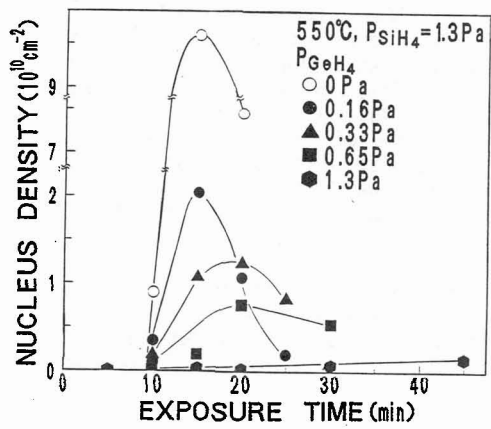


Fig.7.-Dependence of the nucleus density on the time of SiH₄-GeH₄-H₂ exposure of thermal SiO₂ for various GeH₄ partial pressures at a temperature of 550°C, a total pressure 27 Pa and a SiH₄ partial pressure of 1.3 Pa.

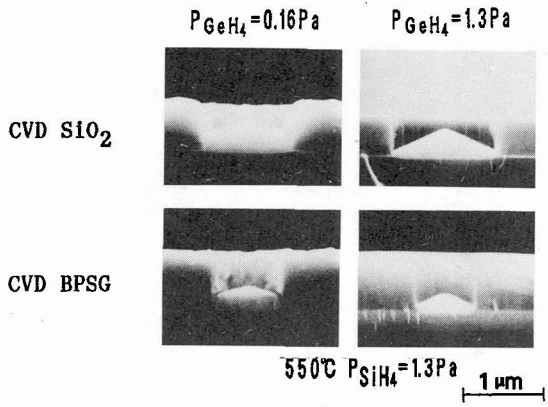


Fig.8.-SEM micrographs of Si-Ge fillings in via-holes opened in CVD SiO₂ and BPSG on Si(100) substrates for various GeH₄ partial pressures at a temperature of 550°C and a SiH₄ partial pressure of 1.3 Pa.

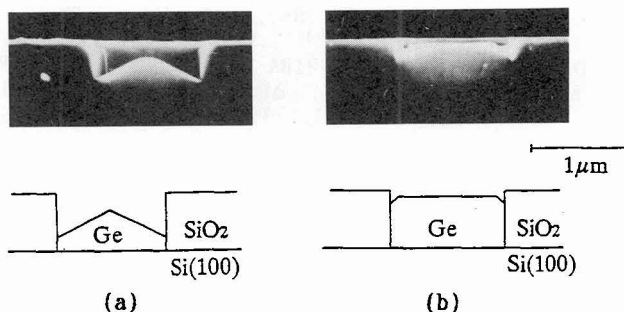


Fig.9.-SEM micrographs of Ge fillings in via-holes opened in CVD- SiO_2 on Si(100) substrates at a deposition temperature of 350°C and a GeH_4 partial pressure of (a) 0.2 Pa and (b) 10 Pa.

It is found that a perfectly selective epitaxy is obtained for CVD boro-phospho-silicate glass /10/.

A perfect selective growth of Ge between Si and SiO_2 was obtained for deposition temperatures of 350°C and 400°C /16/. The selectivity is independent of the partial pressure of GeH_4 and independent of the choice of the carrier gas. This results from ultraclean processing, because selectivity degrades by contamination such as moisture /3/. Two kinds of hole filling behaviors of Ge were found, as shown in figure 9. For lower GeH_4 partial pressures, a regular pyramid-like structure is found, resulting from the formation of facets which have $\{311\}$ surfaces in the $[110]$ direction. Since the surface coverage of GeH_4 on the surface is low for lower GeH_4 partial pressures, as calculated from equation (1), it is suggested that the density of adsorbed species is low enough, and the adsorbed species have enough energy to migrate on the surface making step growth possible, or in other words, the reaction proceeds at steps. On the other hand, for higher GeH_4 partial pressures, no clear facets are found. Since in equation (1) the surface coverage of GeH_4 becomes nearly unity for higher GeH_4 partial pressures, it is suggested that surface migration is restricted either by the lack of energy or by too many nucleation centers due to a large number of reactive species arriving at the surface.

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