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LOW-TEMPERATURE SILICON AND GERMANIUM CVD IN ULTRACLEAN ENVIRONMENT

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Abstract.—Low-temperature Si and Ge CVD processing was investigated under the cleanest possible reaction environment of SiH₄, GeH₄ and H₂ 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 SiH₄ and H₂ partial pressure for Si CVD, and only GeH₄ 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 SiH₄ decomposition induces nucleation on Si oxide. The nucleation rate is suppressed by the presence of GeH₄ and decreases on CVD BPSG compared with SiO₂. Therefore, by a proper choice of deposition temperature, SiH₄ and GeH₄ 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 SiO₂ is obtained. At low surface coverages of GeH₄ 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 SiH₄, GeH₄ and H₂ 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-
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 SiH₄ gas flow and a 340 sccm H₂ 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.

...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 10⁻¹ 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 N₂ purged transfer chamber was combined with the reactor inlet. The wafers, placed on a quartz boat, are transported into the reactor under ultraclean N₂ atmosphere through the transfer chamber. After closing the gate valve, the N₂ flow stops and the reactor tube is purged with high-purity H₂. 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 N₂, H₂ and SiH₄ gases used was 10 ppb or lower and that of GeH₄ 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 H₂SO₄ and H₂O₂ or in hot NH₄OH-H₂O₂-H₂O and hot HCl-H₂O₂-H₂O 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 GeH₄ partial pressure of 1.7 Pa and a deposition temperature of 400°C. Prior to deposition, the substrates were dipped in a H₂O₂ 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 H₂ gas under a pressure of about 200 Pa. 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, 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 SiH₄ and GeH₄. Even for Si deposition at 650°C on the native oxide formed in a hot NH₄OH-H₂O₂-H₂O solution, Si epitaxy was possible. A typical example indicating the reduction of the native oxide on the Si surface by GeH₄ is shown in Figure 3. Here, the native oxide was formed by dipping the samples in a H₂O₂ 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 GeH₄. 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 SiH₄ or GeH₄ 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

\[ R = k n_0 K_A P_A / (1 + K_A P_A^H P_{H2}) \]  

Here, \( k \) is the rate constant for the surface reaction of SiH₄ or GeH₄, \( n_0 \) the adsorption site density at the surface, and \( K_A \) and \( K_H \) are the adsorption equilibrium constants, \( P_A \) and \( P_{H2} \) the SiH₄ or GeH₄ and H₂ partial pressures, respectively. Equation (1) means that, for lower \( P_A \) such as \( 1 >> K_A P_A \), the deposition rate increases proportionally with \( P_A \), while for higher \( P_A \) such as \( 1 << K_A P_A \), the deposition rate is independent of \( P_A \).

For Si deposition in the temperature range 550 - 650°C, the deposition rate is expressed by equation (1). The fitting parameters are weakly dependent on the
substrate orientation, and the deposition rate is limited by the chemisorption of gaseous H₂ 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 H₂ molecules on the Ge surface can be neglected for H₂ 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:

\[ \kappa_{n0}(100) = 6.9 \times 10^{14} \exp(-1.65eV/kT) \]  \hspace{1cm} (A/min) \hspace{1cm} (2)

\[ K_A(100) = 3.3 \times 10^{-10} \exp(1.2eV/kT) \]  \hspace{1cm} (Pa⁻¹) \hspace{1cm} (3)

and for the deposition on Si(111),

\[ \kappa_{n0}(111) = 1.2 \times 10^{15} \exp(-1.65eV/kT) \]  \hspace{1cm} (A/min) \hspace{1cm} (4)
The activation energy of GeH₄ 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 Pₐ, the surface coverage Kₐ/(1 + Kₐ) of GeH₄ 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 Pₐ, the surface coverage is unity for (100) and (111) surfaces and knₐ 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 Kₐ and knₐ were calculated from the deposition data on various differently oriented substrates. For the (100) surface Kₐ 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 nₒ is considered to include not only the hollow bridge site density but also the other dangling bonds, because the value of knₒ, 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 GeH₄ proceeds at adsorption sites composed of dangling bonds on the surface /14/. The large difference in the substrate orientation dependence of knₒ and Kₐ 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 SiH₄ reaction rate increases up to a maximum value and then decreases with increasing GeH₄ 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 GeH₄ reaction rate increases monotonically with GeH₄ partial pressure, it is considered that Si-hydride adsorption is not inhibited by Ge-hydride adsorption. It was also found that the maximum SiH₄ 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 SiH₄ 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.

\[
K_a(111) = 5.5 \times 10^{-11} \exp(1.2eV/kT). \quad \text{(Pa}^{-1}\text{)}
\]

Fig.6.-GeH₄ partial pressure dependence of the SiH₄ reaction rate at a deposition temperature of 550°C, a total pressure of 27 Pa and a SiH₄ 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 SiO$_2$. 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 650°C /15/.

With the addition of GeH$_4$ to SiH$_4$, a suppression of nucleation was found as shown in Figure 7. Since the deposition rate increases drastically with GeH$_4$ 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 SiO$_2$ on Si(100) substrates.

Fig.7.-Dependence of the nucleus density on the time of SiH$_4$-GeH$_4$-H$_2$ exposure of thermal SiO$_2$ for various GeH$_4$ partial pressures at a temperature of 550°C, a total pressure 27 Pa and a SiH$_4$ partial pressure of 1.3 Pa.

Fig.8.-SEM micrographs of Si-Ge fillings in via-holes opened in CVD SiO$_2$ and BPSG on Si(100) substrates for various GeH$_4$ partial pressures at a temperature of 550°C and a SiH$_4$ partial pressure of 1.3 Pa.
It is found that a perfectly selective epitaxy is obtained for CVD boro-phosphosilicate 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 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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