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Atomic Layer Control of Germanium and Silicon on Silicon Using Flash Heating in Ultraclean Chemical Vapor Deposition

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The separation between surface adsorption and reaction of reactant gas on Si substrate was investigated by heating the surface with a Xe flash lamp in an ultraclean low-pressure environment. Using GeH_4 gas, single atomic layer epitaxy of Ge per flash lamp light shot has been realized for some process conditions. It is proposed that the total adsorption site density is nearly equal to the surface atom density, and continuous Ge-hydride adsorption is inhibited on the surface covered with an adsorbed Ge-hydride monolayer. Using SiH_4 and Si_2H_6, atomic layer deposition control of Si was also examined.

1. Introduction

Atomic layer control in CVD is attractive for the progress in future semiconductor devices, e.g. ultrasmall devices and hetero-devices. In conventional CVD, surface adsorption and reaction of reactant gases proceed simultaneously. In order to perform atomic layer control, it is important to separate these two mechanisms. So far, in atomic layer epitaxy[1-4], the self-limiting process of gas adsorption has been employed using metal organic or chloride gases which forms a strong chemical bond between surface atoms and adsorbed molecules. Recently, monolayer growth of Si by Si_2H_6 adsorption and ArF excimer laser irradiation has been investigated[5,6] without using metal organic or chloride gases. However, atomic layer control using simple reactant gases such as SiH_4 and GeH_4 has not been reported. In the present work, the separation between surface adsorption and reaction of such reactant gases on Si substrates was investigated by heating the surface with a Xe flash lamp in an ultraclean low-pressure environment. By this method, atomic layer deposition of Ge and Si per flash lamp light shot has been achieved. In addition, the hydride adsorption mechanisms are discussed.

2. Experimental

The experiment of deposition was carried out using GeH_4 or SiH_4 or Si_2H_6 in an ultraclean RF-heated cold-wall low-pressure CVD system as schematically shown in Fig.1. With gate valves, a turbo molecular pump and load lock chamber, the system is UHV compatible. The samples are set into the load lock chamber and transported into the reactor under ultraclean H_2 purge and evacuation. During evacuation, H_2 gas is flowing continuously to avoid contaminations from the exhaust line[7]. While heating the substrate, the reactant gases are introduced into the reactor and then the hydrides adsorbed at the surface are decomposed by Xe flash lamp light shots (duration about 1msec, 20J/cm^2). The lamp light shots were incident perpendicularly upon substrates at shot to shot intervals of a few tens of seconds. Here, the moisture level of the H_2, SiH_4 and Si_2H_6 gases at the reactor inlet was 10 ppb or lower, and that of GeH_4 was 23 ppb or lower at the reactor inlet. The substrate surface temperature was measured prior the light incidence by an optical pyrometer. The substrates used were 1.25

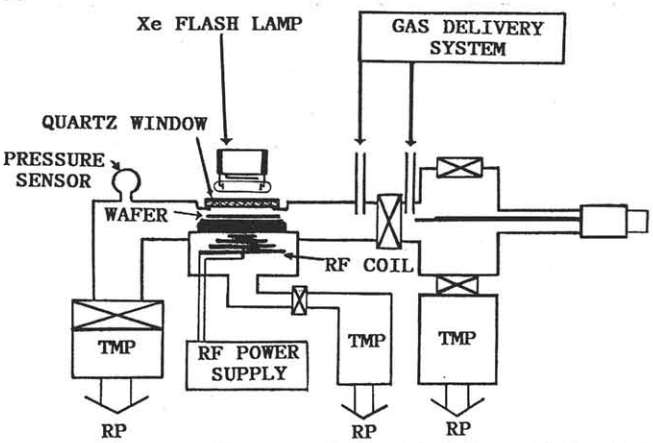

Fig.1 Schematic diagram of an ultraclean RF-heated cold-wall LPCVD system with Xe flash lamp.

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inch-diam p-type wafers of 2-20 Ohm-cm with mirror polished (100), (411), (311), (211), (111) and (011) surfaces. Before loading the wafers into the load lock chamber, they were cleaned in several cycles in a 4:1 solution of H_2SO_4 and H_2O_2, high-purity DI water, and 2% HF. The deposited thickness was measured by a Tencor Alpha Step. The structure of the film surface was evaluated by electron diffraction.

3. Results and discussion

Figure 2 shows the substrate temperature dependence of deposited Ge film thickness per flash lamp light shot. For the 400°C pre-heated samples in the substrate temperature range of 260-275°C the deposited thickness per shot is independent of the substrate temperature and is found to be about 1.4Å on Si(100) and 1.6Å on Si(111), which is nearly equal to the atomic layer thickness of Ge (100) and Ge(111), respectively. This result also means that Ge-hydride molecules of about $6x10^{14}$ and $7x10^{14}cm^{-2}$ are adsorbed at (100) and (111) surfaces, respectively, just before Ge deposition due to a flash lamp light shot. On the other hand, without pre-heating in the same substrate temperature range as the above, Ge deposition due to flash lamp irradiation is not observed in the substrate temperature range of 260-275°C as shown in Fig.2. We believe that GeH_4 adsorption is prevented by impurities adsorbed on the substrate surface without pre-heating. It should be noted that the anomalous increase in the deposited Ge film thickness at higher substrate temperatures above 280°C can be explained by continuous GeH_4 decomposition during the intervals between light shots.

Figure 3 shows the shot to shot interval time dependence of the deposited film thickness per shot on Si(100). It is found that the necessary time for reaching the atomic layer thickness becomes shorter for higher GeH_4 partial pressures. In other words, the surface coverage velocity of Ge-hydrides is higher for higher GeH_4 partial pressures since the ratio of the deposited thickness to the atomic layer thickness is equal to the adsorbed Ge-hydride coverage. From Fig.3, it is also found that the deposited thickness per shot, i.e., the GeH_4 adsorption number at a longer time interval for reaching adsorption equilibrium is independent of the GeH_4 partial pressure. This means that the density of the adsorbed Ge-hydrides becomes nearly equal to that of the surface atoms in the adsorption equilibrium for the investigated GeH_4 partial pressure range. Table I shows the substrate orientation dependence of deposited film thickness per shot, for the shot to shot time interval at which the adsorption equilibrium is reached. The deposited film thickness is in good agreement with the single atomic layer thickness. This result suggests that the total adsorption site density is nearly equal to the surface atom density, and continuous Ge-hydride adsorption on the surface covered with an adsorbed Ge-hydride monolayer is inhibited. As a result, the adsorption of H_2 is negligibly small

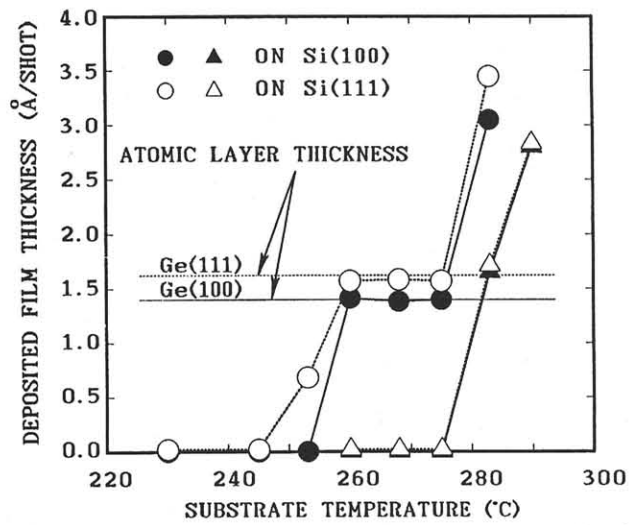

Fig.2 Substrate temperature dependence of the thickness per shot for Ge films. The shot to shot time interval was 20sec, the GeH_4 partial pressure 13Pa, and the total pressure (GeH_4 + H_2) 280Pa. Circles and triangles indicate the samples deposited after a 400°C pre-heating and without a 400°C pre-heating, respectively.

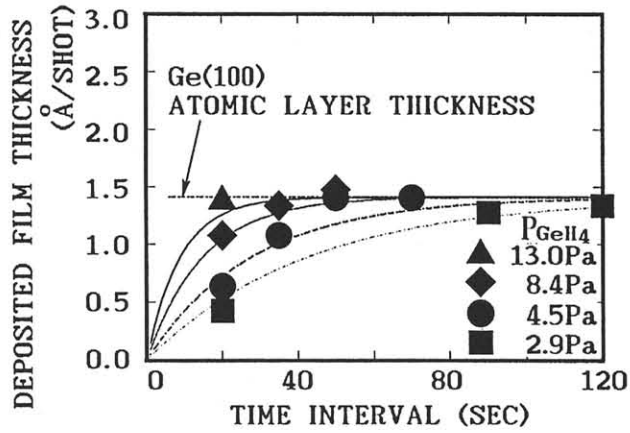

Fig.3 Shot to shot time interval dependence of deposited Ge thickness per shot for various GeH_4 partial pressures on a Si(100) substrate at a substrate temperature of 268°C.

Table I. Substrate orientation dependence of the deposited Ge film thickness per shot, for the shot to shot time interval of 20sec at a substrate temperature of 268°C and a GeH_4 partial pressure of 13Pa.

substrate orientation	deposited thickness per shot (Å)	single atomic layer thickness (Å)	surface atom density ($x10^{14}cm^{-2}$)
(011)	2.0	2.00	8.92
(111)	1.6	1.63	7.27
(211)	1.7	1.73	7.71
(311)	1.6	1.71	7.63
(411)	1.5	1.67	7.45
(100)	1.4	1.41	6.29

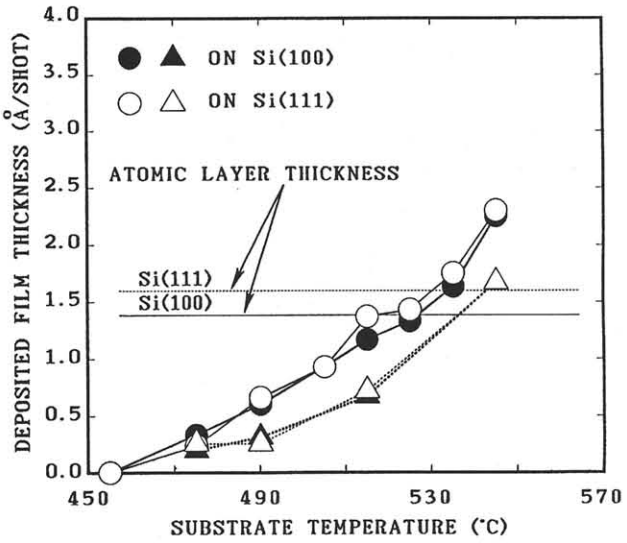

Fig.4 Substrate temperature dependence of the thickness per shot for Si films deposited using SiH_4. The shot to shot time interval was 20sec, the SiH_4 partial pressure 13Pa, and the total pressure (SiH_4 + H_2) 280Pa. Circles and triangles indicate the samples deposited with and without flash lamp light shots, respectively.

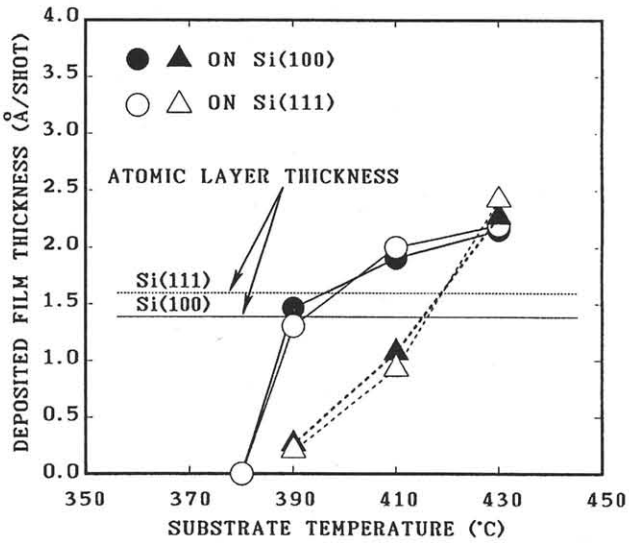

Fig.5 Substrate temperature dependence of the thickness per shot for Si films deposited using Si_2H_6. The shot to shot time interval was 20sec, the Si_2H_6 partial pressure 100 Pa, and the total pressure (Si_2H_6 + H_2) 300 Pa. Circles and triangles indicated the samples deposited with and without flash lamp light shots, respectively.

compared with the Ge-hydride adsorption[8], and the total adsorption site density is equal to the surface site density.

In the case of Si deposition, continuous decomposition during shot to shot interval is not negligible because of the performance limit of the flash lamp under the investigated conditions. Figure 4 shows the substrate temperature dependence of the thickness per flash lamp light shot for Si films deposited using SiH_4, together with the thickness of the films deposited continuously during shot to shot interval. Subtracting the continuous deposition factor, on average a deposition of about 0.5Å is obtained with one flash lamp light shot. It is considered that the Si-hydride surface coverage decreases by continuous decomposition, and also Si-hydride adsorption is suppressed by H_2 adsorption[9] which is different from Ge-hydride adsorption. The result using Si_2H_6 is shown in Fig. 5. In a certain temperature region, a flash lamp light shot effect of about 1.3Å/shot is observed. At higher temperatures, the agreement between the thicknesses with and without flash lamp light shot may suggest that Si-hydride surface coverage becomes very small compared with the value at high temperatures.

From electron diffraction pattern, single-crystallinity was found for atomic layer controlled Ge films deposited on Si (100), (211), (311), (411) and (011) surfaces. However, on Si(111) surface, a halo pattern was observed under all investigated conditions. On the other hand, in the case of Si deposition almost all samples show an amorphous pattern. Therefore, further investigations about crystal quality as well as surface cleaning are needed.

4. Conclusions

The mechanisms of surface adsorption and reaction of GeH_4 on Si substrates were separated by heating the surface with a Xe flash lamp in an ultraclean low-pressure environment. Single atomic layer epitaxy per flash lamp light shot has been achieved. It is proposed that the total adsorption site density is nearly equal to the surface atom density, and continuous Ge-hydride adsorption is inhibited on the surface covered with an adsorbed Ge-hydride monolayer. In the case of Si deposition, the atomic layer control is possible, but in order to perform single atomic layer epitaxy per shot, further investigations are needed.

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