CONTROL OF GERMANIUM ATOMIC LAYER FORMATION ON SILICON USING FLASH HEATING IN GERMANIUM CVD

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CONTROL OF GERMANIUM ATOMIC LAYER FORMATION ON SILICON USING FLASH HEATING IN GERMANIUM CVD

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Abstract.-The separation between surface adsorption and reaction of GeH_4 on a Si substrate was investigated by heating the surface with a Xe flash lamp in an ultraclean low-pressure environment. The GeH_4 partial pressure dependence of the deposited Ge thickness and relationship between atomic layer thickness and the shot to shot time interval have been investigated. Single atomic layer deposition per flash lamp light shot has been realized for some process conditions. From electron diffraction patterns, a single-crystallinity was found for most substrate orientations.

1.-Introduction.

Atomic layer control in CVD is attractive for 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(ALE) of II-VI and III-V compound semiconductor materials/1,2/, the self-limiting process of gas adsorption has been employed using metal organic or chloride gases which form a strong chemical bond between surface atoms and adsorbed molecules. Similar methods have been carried out in Ge and Si ALE using $Ge(C_2H_5)_2H_2$/3,4/ and $SiCl_2H_2$/5/. Recently, without using metal organic or chloride gases, monolayer growth of Si by Si_2H_6 adsorption and ArF excimer laser irradiation has been reported/6,7/. 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 GeH_4 on a Si substrate was investigated by heating the surface with a Xe flash lamp in an ultra-clean low-pressure environment, and atomic layer control of Ge has been realized.

2.-Experimental.

The Ge deposition was carried out in an ultraclean RF-heated cold-wall low-pressure CVD system. Figure 1 shows the system schematically. With gate valves, a turbo molecular pump system and load lock chamber, the system is ultrahigh vacuum compatible. The samples are placed in the load lock chamber and transported into the reactor under ultraclean H_2 purge and evacuation. During evacuation, hydrogen gas is continuously flowing to avoid contamination from the exhaust line./8/ Deposition time sequence after the samples were placed on the susceptor in the reactor is shown in Figure 2. The samples are pre-heated up to 400 ^{o}C to desorb the impurities adsorbed on the substrate surface as described below. Then, the samples are cooled down to the deposition temperature and GeH_4 is introduced into the reactor.

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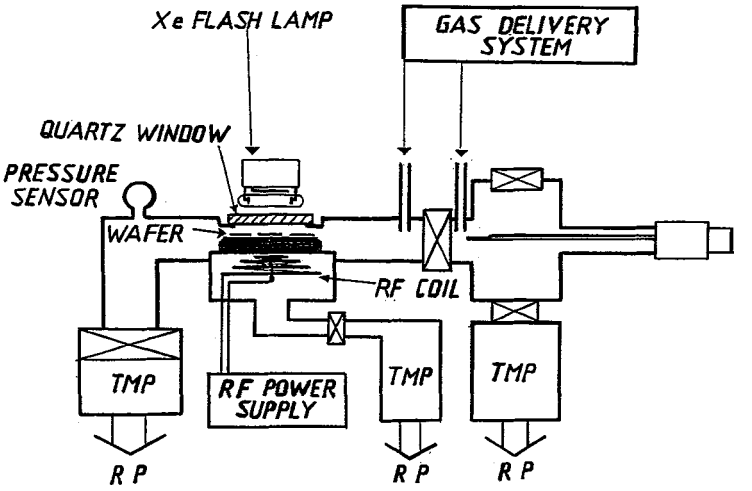

Fig.1.-Schematic diagram of an ultraclean RF-heated cold-wall low-pressure CVD system with Xe flash lamp.

Under a total pressure (GeH_4 + H_2) of about 280Pa and substrate surface temperatures between 230 and 290°C, in which GeH_4 decomposition was not observed, Ge hydride adsorbed at the surface was decomposed with Xe flash lamp light shots(1msec, 20J/cm^2). The lamp light shots were perpendicularly incident upon substrates at shot to shot intervals of a few tens of seconds. Here, the moisture levels of H_2 and GeH_4 gases used 10 ppb or lower and 23 ppb or lower at the point-of-use, respectively. The substrate surface temperature was measured with an optical pyrometer before exposing to incident light. The substrates used were 1.25 inch-diam p-type wafers of 2-20 Ohm-cm with a mirror finish (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 surfaces was evaluated by electron diffraction.

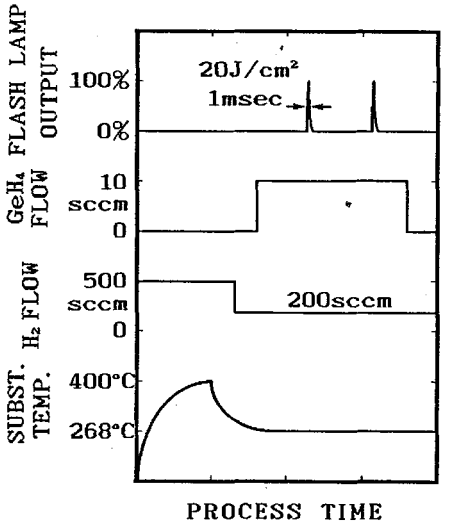

Fig.2.-Typical deposition time sequence after setting the samples on the susceptor in the reactor.

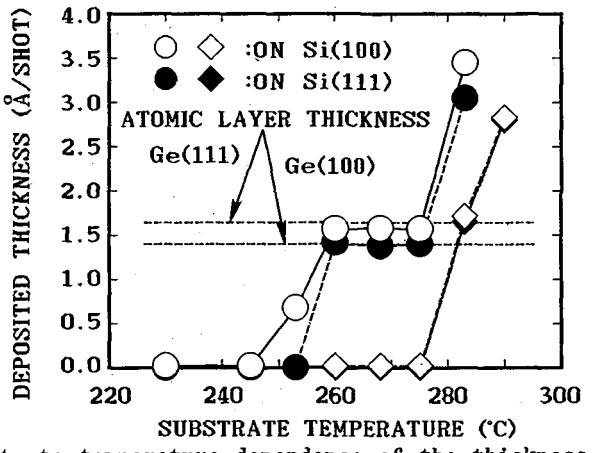

Fig.3.-Substrate temperature dependence of the thickness per shot for Ge films deposited on Si(100) and (111) substrates with 150 shots. The shot to shot time interval was 20 sec, and the GeH_4 partial pressure 13 Pa. Circles and diamonds indicate the samples deposited after a 400 ^oC pre-heating and without a 400 ^oC pre-heating, respectively.

3.-Results and discussion.

Figure 3 shows the substrate temperature dependence of deposited film thickness per flash lamp light shot. For the 400 ^oC pre-heated samples, in the substrate temperature range 260-275^oC, 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 are nearly equal to the atomic layer thickness of Ge(100) and Ge(111), respectively. This result also means that Ge-hydride molecules of about 6 x 10^{14} and 7 x 10^{14} cm^{-2} are adsorbed at (100) and (111) surfaces, respectively, just before the Ge deposition due to a flash lamp light shot. On the other hand, without pre-heating, Ge deposition due to flash lamp irradiation is not observed in the substrate temperature range 260-275^oC as shown in Figure 3. We believe that GeH_4 adsorption is prevented by impurities adsorbed on the substrate surface without pre-heating. Here, it should be noted that, in the present experiments, Ge deposition on SiO_2 was not observed. The anomalous increase in deposited film thickness at higher substrate temperatures above 280^oC can be explained by continuous GeH_4 decomposition due to an increase in substrate surface temperature during shot to shot.

Figures 4 and 5 show the shot to shot interval time dependence of deposited film thickness per shot on Si(100) and Si(111). It is found that the time for reaching the atomic layer thickness becomes shorter at higher GeH_4 partial pressure. In other words, the surface coverage velocity of Ge-hydride is higher at higher GeH_4 partial pressure since the ratio of deposited thickness to the atomic layer thickness is equal to adsorbed Ge-hydride coverage. Now, assuming that GeH_4 is adsorbed at single adsorption site, the total adsorption site density at surface is given by

$$n_o = Q_s + Q_{GeH4}. \qquad (1)$$

Here Q_s is the density of surface sites, where GeH_4 and other species are not adsorbed, and Q_{GeH4} is the site density of adsorbed GeH_4. It is also assumed that hydrogen adsorption is negligibly small compared with Q_s and Q_{GeH4}./9/ Then, the surface coverage velocity is given by

$$dQ_{GeH4}/dt = k_1 P_{GeH4} Q_s - k_{-1} Q_{GeH4}$$

$$= k_1 P_{GeH4} n_o - (k_1 P_{GeH4} + k_{-1}) Q_{GeH4}, \quad (2)$$

where k_1 and k_{-1} are the rate constants of GeH_4 adsorption and desorption, respectively, P_{GeH4} the GeH_4 partial pressure. The integration of equation (2) gives

$$Q_{GeH4} = (k_1 P_{GeH4} n_o)/(k_1 P_{GeH4} + k_{-1})[1 - \exp\{ - (k_1 P_{GeH4} + k_{-1})t\}]. \quad (3)$$

Figures 4 and 5 show that the deposited thickness per shot, i.e., amount of GeH_4 adsorption at a longer time interval for reaching adsorption equilibrium, is independent of P_{GeH4}, so that k_{-1} is negligibly small compared with $k_1 P_{GeH4}$. Therefore, $Q_{GeH4} = n_o$ is obtained for the adsorption equilibrium in the investigated GeH_4 partial pressure range. The results(solid curves shown in the Figures 4 and 5) calculated from equation (3) with $k_1 = 8.3 \times 10^{-3}$ /Pa/sec are in good agreement with the experimental data. These results also mean that the rate constant of GeH_4 adsorption is independent of the substrate orientation.

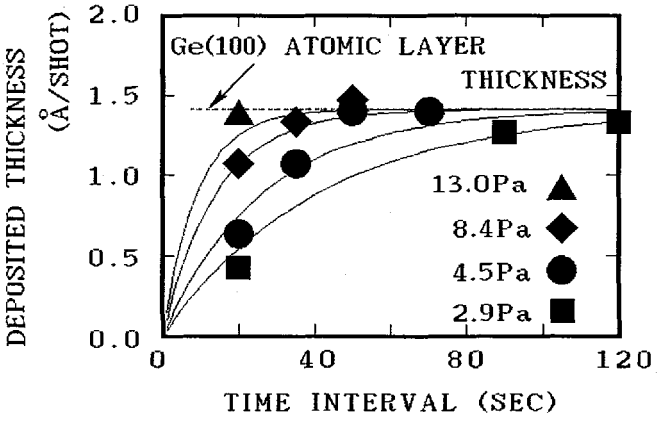

Fig.4.-Shot to shot time interval dependence of deposited Ge thickness per shot for various GeH_4 partial pressures. Ge film was deposited on a Si(100) substrate with 150 shots. The deposition temperature was 268 °C.

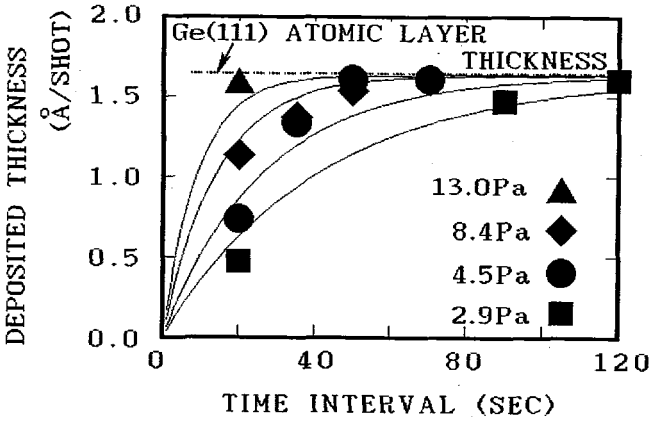

Fig.5.-Shot to shot time interval dependence of deposited Ge thickness per shot for various GeH_4 partial pressures. Ge film was deposited on a Si(111) substrate with 150 shots. The deposition temperature was 268 °C.

Table I.-Substrate orientation dependence of the deposited Ge film thickness per shot, for the shot to shot time interval of 20 sec where the adsorption equilibrium was reached. The Ge films were deposited with 150 shots at the deposition temperature of 268 ^{o}C and the GeH_4 partial pressure of 13 Pa.

substrate orientation	deposited thickness per shot (Å)	deposited amount of Ge per shot ($x10^{14}cm^{-2}$)	single atomic layer thickness (Å)	surface atom density ($x10^{14}cm^{-2}$)
(011)	2.0	8.9	2.00	8.92
(111)	1.6	7.1	1.63	7.27
(211)	1.7	7.6	1.73	7.71
(311)	1.6	7.1	1.71	7.63
(411)	1.5	6.7	1.67	7.45
(100)	1.4	6.2	1.41	6.29

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 is inhibited on the surface covered with an adsorbed Ge-hydride monolayer. A typical electron diffraction pattern of a Ge film deposited on Si(100) substrate is shown in Figure 6. The dot pattern, indicating single-crystallinity, was found, and similar results were obtained for films on Si(211), (311), (411) and (011) oriented substrates. However, on Si(111), a halo pattern was observed. Therefore, further investigations about the crystal quality have to be carried out.

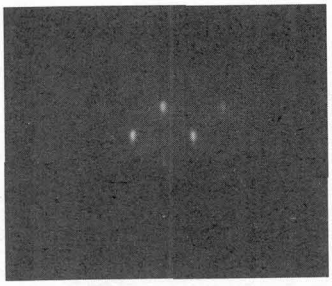

Fig.6.- Electron diffraction pattern for Ge film deposited on Si(100) substrate with 150 shots. The shot to shot time interval was 20 sec, the deposition temperature 268 ^{o}C and the GeH_4 partial pressure 13 Pa.

4.-Conclusions.

The processes 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 deposition per flash lamp light shot has been

realized. 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.

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