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Initial Growth Stages of Si on Ge and Ge on Si for Atomic-Layer Epitaxy Control Using SiH_4 and GeH_4 Gases

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Initial growth stages of atomic-layer heteroepitaxy in the flash-heating chemical vapor deposition using SiH_4 and GeH_4 gases were investigated. It was found that Si was deposited on the Ge surface even at substrate temperatures below 300 °C without the flash shot, and the deposited Si thickness increased with increasing the SiH_4 exposure time and saturated to a single atomic-layer thickness with a longer time to reach saturation at the substrate temperature range of 200–300 °C. In the case of initial Ge growth on the wet-cleaned Si surface, by increasing the flash light intensity and the GeH_4 partial pressure, the incubation period was reduced and a single atomic-layer growth of Ge on the Si(100) was achieved with a single flash shot at the substrate temperature of 275 °C.

1. Introduction

Atomic-layer epitaxy control of Si and Ge by chemical vapor deposition (CVD) is attractive for the fabrication of novel heterostructure devices, e.g. quantum well or superlattice structure devices. In order to achieve atomic-layer epitaxy control, it is important to separate adsorption and reaction of reactant gases. 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 form strong chemical bonds between surface atoms and adsorbed molecules. However, in order to prevent any contamination into deposited films, simple hydride gases such as SiH_4 and GeH_4 without carbon or halogen should be used as a reactant gas. In our previous work [5-8], the separation between the surface adsorption and the reaction of SiH_4 or GeH_4 on a Si substrate was achieved using a flash-heating CVD system, where the reactant molecules adsorbed on the surface were decomposed by the Xe flash lamp light shots with the intensity of 20 J/cm^2. These results gave us informations about SiH_4 adsorption on Si and GeH_4 adsorption on Ge, respectively. However, adsorption processes of SiH_4 on the Ge surface and GeH_4 on the Si surface in the initial growth stages were not clear.

In the present work, in order to control atomic-layer heteroepitaxies of Si on the Ge surface and Ge on the Si surface, the initial growth stages in atomic-layer epitaxy using SiH_4 and GeH_4 gases were investigated.

2. Experimental

The Si and Ge depositions were carried out by using SiH_4 and GeH_4 gases, respectively, in an ultraclean rf-heated, cold-wall low-pressure flash-heating CVD system as reported before [5-8]. The flash light was irradiated upon the substrate surface perpendicularly with the time interval of a few tens seconds, its duration was about 1 ms and the intensity was varied from 20 to 60 J/cm^2, as shown in Fig.1. The substrates used were p-type Si wafers of 2–20 Ωcm with mirror-polished (100) surface. Before loading the substrates 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 deionized (DI) water, 2% HF with a final rinse in DI water (hereafter referred as wet-cleaned Si(100)). As the substrate for Si growth on the Ge surface, a 400Å-thick Ge epitaxial film was deposited by thermal decomposition of GeH_4 at 350 °C on the wet-cleaned Si(100) substrate, and it was cleaned in 2% HF solution with a final rinse in DI water (hereafter referred as wet-cleaned Ge(100)). Thicknesses of the Si and Ge films were measured by Tencor Alpha Step. The ultrathin film thicknesses of Si on the Ge

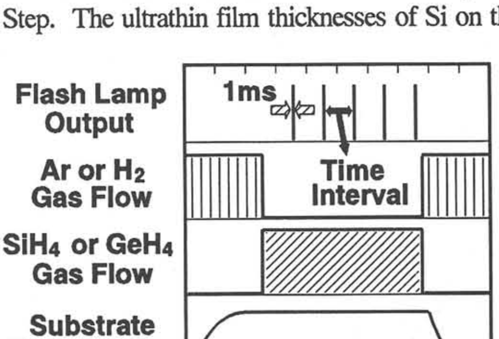

Fig.1. Typical process sequence of the flash-heating CVD after the samples were placed on the susceptor in the reactor.

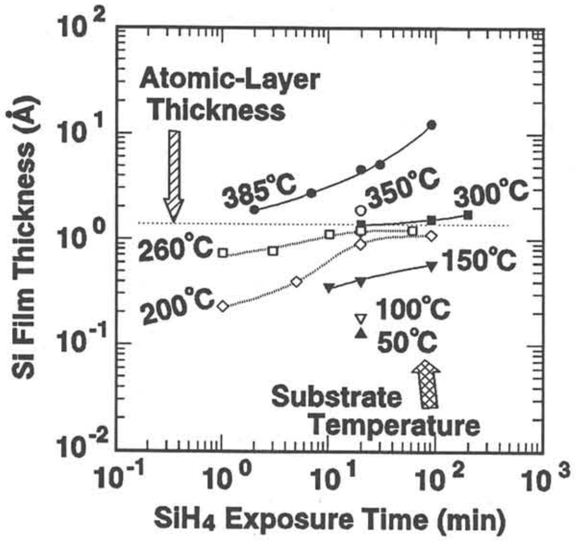

Fig.2. SiH_4 exposure time dependence of the Si film thickness deposited on the wet-cleaned Ge(100) at various substrate temperatures without the flash shot. The SiH_4 partial pressure was 500 Pa. Prior to exposing the wet-cleaned Ge(100) to SiH_4 environment, it was heated for 40 minutes in H_2 environment of 290 Pa at a temperature of 260 °C, where the single atomic-layer epitaxy of Ge on the Ge surface was realized by using the flash-heating CVD [7,8]. The Si film thicknesses were determined by XPS.

surface and Ge on the Si surface were also estimated by x-ray photoelectron spectroscopy (XPS).

3. Results and Discussion

3.1. Si Atomic-Layer Growth on the Ge Surface

Figure 2 shows the SiH_4 exposure time dependence of the Si film thickness deposited on the wet-cleaned Ge(100) without the flash shot. It is found that a Si film is deposited on the Ge surface without the flash shot even at temperatures below 385 °C, where the continuous thermal reaction of SiH_4 on the Si surface scarcely occurs (deposition rate below 0.1 Å/minute) [5,6]. This may result from larger hydrogen desorption on the Ge surface than that on the Si surface [9,10]. At a temperature range of 200–300 °C, it is clear that the deposited Si film thickness increases with increasing SiH_4 exposure time and saturates to the single-atomic layer thickness with a longer time to reach saturation at a lower temperature, i.e., the SiH_4 reaction rate on the initial Ge surface is much larger than that on the Ge surface covered with a single atomic-layer of Si.

At a temperature of 385 °C, it is expected that the single atomic-layer formation of Si may be also realized by reducing the SiH_4 exposure time below 1 minute, although the Si film thickness increases continuously beyond the single-atomic layer thickness. It is considered that enhancement of the SiH_4 reaction beyond the single atomic-layer thickness is caused by the reaction with Ge atoms segregated on the top surface, although the Ge segregation was reported only at higher temperatures [11]. The surface segregation of Ge atoms would result in degradation of the abruptness of the Si/Ge heterointerface. Therefore, the deposition process under the low-temperatures below ~300 °C, where the surface segregation does not proceed, is necessary.

3.2. Ge Atomic-Layer Growth on the Si Surface

Figure 3 shows the dependence of the Ge film thickness deposited on wet-cleaned Si(100) on the number of the flash shots. After the substrate has been once pre-heated up to 400 °C in the reactor, the Ge single atomic-layer epitaxy per shot is realized with the flash light intensity of 20 J/cm^2, as already reported at 260–275 °C [7,8]. Without pre-heating, on the other hand, the incubation period of Ge growth during a few hundreds of flash shots is observed with the flash light intensity of 20 J/cm^2. Since a dihydride phase of the Si(100) surface is transformed into a mono-hydride phase by heat treatment up to ~400 °C as is well known [10], the above difference by pre-heating means that the adsorption of GeH_4 molecules onto the Si surface and/or the reaction of the adsorbed GeH_4 molecules on the Si surface by the flash light shot is dependent on the hydrogen coverage of the Si surface. Furthermore, it is also found that the incubation period on the wet-cleaned Si surface is reduced to a few tens of shots by increasing the intensity up to 60 J/cm^2 even without the pre-heating. The incubation period hardly decreased by a repetition of additional 100 flash shots with the intensity of 60 J/cm^2 prior to an introduction of GeH_4 gas into the reactor. This means that the flash shot scarcely induces the hydrogen desorption from the Si surface in the absence of GeH_4 gas at the surface.

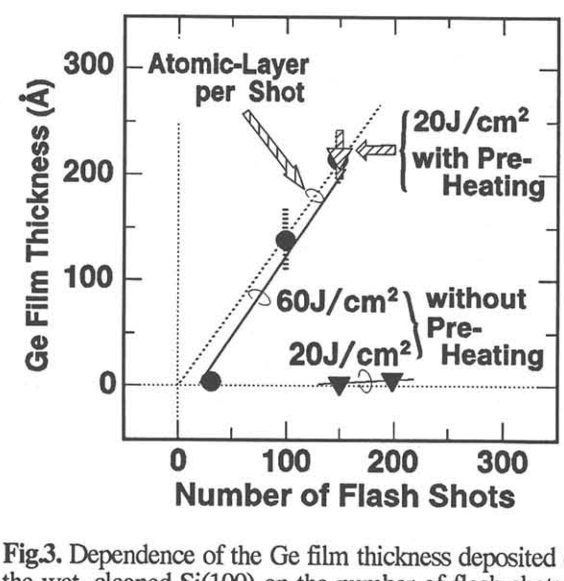

Fig.3. Dependence of the Ge film thickness deposited on the wet-cleaned Si(100) on the number of flash shots at a substrate temperature of 260 °C. The GeH_4 partial pressure was 23 Pa and the shot to shot time interval 40 s.

Figure 4 shows the GeH_4 exposure time dependence of the Ge film thickness deposited on wet-cleaned Si(100) with a single flash shot of 60 J/cm^2 at a substrate temperature of 275 °C without the pre-heating. It is found that a Ge layer is certainly formed at the GeH_4 partial pressure of 300 Pa and 500 Pa by the single flash shot on the wet-cleaned Si surface, and its thickness increases and saturates to the single atomic-layer thickness with increasing the GeH_4 exposure time. Therefore, it is assumed that all the adsorbed Ge containing species at the surface are decomposed perfectly by the flash shot of 60 J/cm^2. Then, the deposited thickness per shot (d_L) can be expressed by the Langmuir adsorption type equation [5,6,8]:

$$d_L = d_{Ge}\,\frac{n_0}{N}\,\frac{k_{GeH4}P_{GeH4}}{k_{GeH4}P_{GeH4}+k_{-GeH4}} \times[1-\exp\{-(k_{GeH4}P_{GeH4}+k_{-GeH4})\tau\}]\,, \qquad (1)$$

where d_{Ge} is the atomic-layer thickness of Ge, n_0 the surface adsorption site density, N the surface atom density, k_{GeH4} and k_{-GeH4} the rate constants of GeH_4 adsorption and desorption, respectively, P_{GeH4} the GeH_4 partial pressure and τ the GeH_4 exposure time. Substituting the experimental data into Eq.(1) and neglecting k_{-GeH4} with d_{Ge}=1.4 Å and $n_0=N$ [5-8], k_{GeH4} is obtained to be 1.3×10^{-5} Pa^{-1} s^{-1}. The k_{GeH4} value on the Si surface obtained here is much lower than that on the Ge surface (8.3×10^{-3} Pa^{-1} s^{-1} at 268 °C [8]). As mentioned before, it is expected that the GeH_4 adsorption is influenced by the different hydrogen coverage of the Si surface from that of the Ge surface. Further investigation is necessary for the relationship between the adsorption rate constant and the hydrogen coverage of the surface.

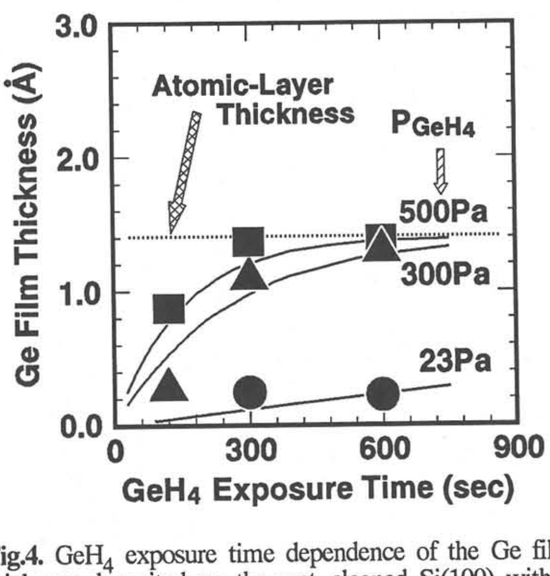

Fig.4. GeH_4 exposure time dependence of the Ge film thickness deposited on the wet-cleaned Si(100) with a single flash shot at a substrate temperature of 275 °C without the pre-heating. The flash light intensity was 60 J/cm^2. The Ge film thicknesses were determined by XPS. The solid curves are calculated from Eq.(1) with $k_{GeH4}=1.3\times10^{-5}$ Pa^{-1} s^{-1}.

4. Conclusions

In the initial growth stages in atomic-layer epitaxy using SiH_4 and GeH_4 gases were investigated for atomic-layer heteroepitaxy. The SiH_4 reaction on the Ge surface induces a single atomic-layer formation of Si even without the flash shot under the low-temperature conditions below 300 °C, where the SiH_4 reaction on the Si surface scarcely proceeds. The Ge single atomic-layer growth on the Si surface is achieved by a single flash shot in the GeH_4 partial pressure of a few hundreds Pa and with the high flash light intensity of 60 J/cm^2 at a substrate temperature of 275 °C.

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