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Atomic Layer-by-Layer Epitaxy of Silicon and Germanium Using Flash Heating in CVD

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Abstract. Atomic layer-by-layer epitaxy control of Si and Ge in flash-heating CVD using SiH_4 and GeH_4 gases was investigated. Self-limiting SiH_4 reaction on the Ge surface results in Si atomic-layer formation at substrate temperatures below 300 °C even without the flash heating. In the case of Ge growth, by increasing the flash light intensity and the GeH_4 partial pressure, Ge atomic-layer growth on the wet-cleaned Si(100) was achieved with a single flash shot at 275 °C. Using these growth controls, resonant tunneling diodes of Ge / $\text{Si}_1\text{Ge}_1(50\text{\AA})$ / Ge(50Å) / $\text{Si}_1\text{Ge}_1(50\text{\AA})$ / Ge, in which the Si_1Ge_1 layers were formed by alternately depositing single atomic-layers of Si and Ge, were fabricated, and clear negative resistance in the current-voltage characteristic was observed at 10 K. The current peaks were expected to be assigned to a hole resonant tunneling via light-hole bound state in the Ge quantum well. This fact suggests that the diode structure has abrupt $\text{Si}_1\text{Ge}_1/\text{Ge}$ interfaces by employing a low-temperature atomic layer-by-layer growth process below 300 °C.

1. INTRODUCTION

Atomic layer-by-layer epitaxy control of Si and Ge by chemical vapour deposition (CVD) is attractive to create novel functional nano-structures and superlattice structures by alternately depositing single atomic-layers of the different elements. In order to achieve atomic-layer epitaxy control, it is important to separate the adsorption and reaction of reactant gases. A self-limiting process using metal organic or chloride gases has been employed in atomic-layer epitaxy [1–4]. 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 on Si or GeH_4 on Ge 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 an intensity of 20 J/cm². These results give information about SiH_4 adsorption on Si and GeH_4 adsorption on Ge. However, adsorption processes of SiH_4 on the Ge surface and GeH_4 on the Si surface in the initial growth stages should be studied for atomic layer-by-layer control in the formation of superlattice structures.

In the present work, single atomic-layer growth of Si on the Ge surface and of Ge on the Si surface were investigated and a resonant tunneling diode of Ge / $\text{Si}_1\text{Ge}_1(50\text{\AA})$ / Ge(50Å) / $\text{Si}_1\text{Ge}_1(50\text{\AA})$ / Ge structure was fabricated.

2. EXPERIMENTAL

Single atomic-layer growth of Si and Ge were carried out by use of SiH_4 and GeH_4 gases, respectively, in an ultraclean rf-heated, cold-wall low-pressure CVD system as schematically shown in Figure 1 [5–8]. The typical process sequence of the flash-heating CVD is shown in Figure 2. The flash light duration was about 1 ms and the intensity was varied from 20 to 60 J/cm^2 . The substrates used were p-type Si wafers of 2–20 Ωcm with mirror-polished (100) surface, and they were cleaned in a 4:1 solution of H_2SO_4 (98%) and H_2O_2 (30%) followed by a rinse in high purity deionized (DI) water in several cycles, and a 2% HF solution followed by a final rinse in DI water (hereafter referred as wet-cleaned Si(100)), before loading the substrates into the load-lock chamber. 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 [9], and it was cleaned in a 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 a step profiler. The ultrathin film thicknesses of Si on the Ge surface and Ge on the Si surface were also estimated by x-ray photoelectron spectroscopy(XPS). The fabrication process of resonant tunneling diode of Ge / Si_1Ge_1 (50Å) / Ge(50Å) / Si_1Ge_1 (50Å) / Ge structure is detailed in Section 3.3.

Figure 1: Schematic diagram of the ultraclean rf-heated cold-wall low-pressure CVD system with a Xe flash lamp.

Figure 2: Typical process sequence of the flash-heating CVD after the samples were placed on the susceptor in the reactor.

3. RESULTS AND DISCUSSION

3.1 Single Atomic-Layer Growth of Si on the Ge surface

Figure 3 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 thermally deposited on the Ge surface even at temperatures below 385 °C, where the continuous thermal reaction on the Si surface scarcely occurs [5,6]. At 200–300 °C, it is found that the deposited Si film thickness increases with increasing SiH_4 exposure time and saturates to the single atomic-layer thickness, i.e., the SiH_4 reaction rate on the initial

Figure 3: 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 260 °C, where the single atomic layer-by-layer epitaxy of Ge on the Ge surface was realized by using the flash-heating CVD [7,8].

Figure 4: SiH_4 exposure time dependence of the Si film thickness deposited on the wet-cleaned Ge(100) at various SiH_4 partial pressure without the flash shot. The substrate temperature was 260 °C. 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 260 °C. The solid curves are calculated from Equation (1) with $k_{\text{GeH}_4} = 1.3 \times 10^{-5} \text{ Pa}^{-1} \text{ s}^{-1}$.

Ge surface is much larger than that on the Ge surface covered with a single atomic-layer of Si. This may be caused by change of the hydrogen adsorbed surface structure [10,11]. At 385 °C, the Si film thickness increases continuously beyond the single-atomic layer thickness. This is considered to be caused by the reaction of SiH₄ at Ge atoms segregated on the top surface, although Ge segregation was reported only at higher temperatures [12]. The surface segregation of Ge atoms would result in degradation of the abruptness of the Si/Ge heterointerface. Therefore, the deposition process below ~300 °C, where the surface segregation does not proceed, is necessary.

Figure 4 shows the SiH₄ exposure time(*t*) dependence of the Si film thickness deposited on the wet-cleaned Ge(100) without flash shot at various SiH₄ partial pressures. Substrate temperature is 260 °C. When the experimental data plotted in Figure 4 were normalized to (*P*_{SiH₄} · *t*) dependence, they were very closely located on the single curve and the thickness at (*P*_{SiH₄} · *t*)~0 was around 0.4 Å with little dependence on *P*_{SiH₄}. Therefore, two-step process, in which there were a fast step and a slow step in reaction kinetics, was distinguished. Assuming that the initial fast growth step with a thickness(*d*_i) proceeded in a short time within a minute, the second step thickness(*d*_S) can be fitted into Langmuir type adsorption equation:

$$d_S = (d_{Si} - d_i) \{1 - \exp(-k_{SiH_4} P_{SiH_4} t)\} , \quad (1)$$

where *d*_{Si} is the single atomic-layer thickness of Si(100), *k*_{SiH₄} the rate constant of SiH₄ adsorption and *P*_{SiH₄} the SiH₄ partial pressure. The solid curves in Figure 4, calculated using the *k*_{SiH₄} value of 3.9×10⁻⁶ Pa⁻¹ s⁻¹, are in very good agreement with experimental data. As far as initial step reaction kinetics, further investigation should be done.

3.2 Single Atomic-Layer Growth of Ge on the Si surface

Figure 5 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 growth per shot is realized with the flash light intensity of 20 J/cm², 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/cm². Since a dihydride

Figure 5: Dependence of the Ge film thickness deposited on the wet-cleaned Si(100) on the number of flash shots at 260 °C. The GeH₄ partial pressure was 23 Pa and the shot to shot time interval 40 s.

Figure 6: GeH₄ exposure time dependence of the Ge film thickness deposited on the wet-cleaned Si(100) with a single flash shot at 275 °C without the pre-heating. The flash light intensity was 60 J/cm². The solid curves are calculated from Equation (2) with $k_{\text{GeH}_4} = 1.3 \times 10^{-5} \text{ Pa}^{-1} \text{ s}^{-1}$.

phase of the Si(100) surface is transformed into a monohydride phase by heat treatment up to ~400 °C as is well known [11], the above difference by pre-heating means that the adsorption of GeH₄ molecules onto the Si surface and/or the reaction of the adsorbed GeH₄ molecules on the Si surface by the flash light shot is dependent on the hydrogen coverage of the Si surface. From Figure 5, 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/cm² even without the pre-heating. The incubation period hardly decreased by a repetition of additional 100 flash shots prior to an introduction of GeH₄ gas into the reactor. This means that the flash shot scarcely induces the hydrogen desorption from the Si surface, i.e., the dihydride phase of Si(100) is not converted into the monohydride phase. Consequently, it is considered that the reaction between the adsorbed GeH₄ molecules and the dihydride Si surface proceeds by the flash shots with the intensity of 60 J/cm².

Figure 6 shows the GeH₄ exposure time dependence of the Ge film thickness deposited on wet-cleaned Si(100) with a single flash shot of 60 J/cm² at a substrate temperature of 275 °C without pre-heating. It is found that the deposited Ge thickness tends to saturate to the single atomic-layer thickness with increasing the GeH₄ exposure time and this results indicate that the surface adsorption site density is equal to the surface atom density. Therefore, it is assumed that all the adsorbed Ge containing species at the surface are decomposed perfectly by the flash shot of 60 J/cm². Then, the deposited thickness per shot (d_L) can be expressed by the Langmuir adsorption type equation [5,6,8]:

$$d_L = d_{\text{Ge}} \frac{k_{\text{GeH}_4} P_{\text{GeH}_4}}{k_{\text{GeH}_4} P_{\text{GeH}_4} + k_{-\text{GeH}_4}} [1 - \exp \{ -(k_{\text{GeH}_4} P_{\text{GeH}_4} + k_{-\text{GeH}_4}) t \}], \quad (2)$$

where d_{Ge} is the atomic-layer thickness of Ge(100), k_{GeH_4} and $k_{-\text{GeH}_4}$ the rate constants of GeH₄ adsorption and desorption, respectively, P_{GeH_4} the GeH₄ partial pressure and t the GeH₄ exposure time. Substituting the experimental data into Equation (2) and neglecting $k_{-\text{GeH}_4}$ with $d_{\text{Ge}} = 1.4 \text{ Å}$ [5–8], k_{GeH_4} is obtained to be $1.3 \times 10^{-5} \text{ Pa}^{-1} \text{ s}^{-1}$. The k_{GeH_4} value on the Si surface obtained here is much lower than that on the Ge surface ($8.3 \times 10^{-3} \text{ Pa}^{-1} \text{ s}^{-1}$ at 268 °C [8]). As mentioned before, it is expected that the GeH₄ adsorption is influenced by the different hydrogen adsorption structure of the Si surface from that of the Ge surface.

3.3 Fabrication of Resonant Tunneling Diode Using Atomic Layer-by-Layer Growth Control

As shown in Sections 3.1 and 3.2, using SiH_4 and GeH_4 gases, self-limited control in single atomic-layer growth was realized. Resonant tunneling diodes, which contain a 50Å-thick Ge quantum well(QW) sandwiched by double barriers of 50Å-thick Si_1Ge_1 atomic-layer superlattice on a relaxed Ge buffer layer, have been fabricated by using our atomic layer-by-layer epitaxy control method at 260–275 °C. Figure 7 shows the schematic cross section of the resonant tunneling diode structure grown on Si(100). As a buried conducting layer and a top contact layer for metal contacts on each side of the double barrier structure, B-doped p^+Ge layers were epitaxially grown on pSi(100) by ultraclean low-pressure CVD using GeH_4 , B_2H_6 and H_2 gases [13]. After loading the $\text{p}^+\text{Ge}/\text{pSi}(100)$ substrates into the flash-heating CVD reactor shown in Figure 1, a 200Å-thick Ge buffer layer was grown by thermal decomposition of GeH_4 at 350 °C. As a QW layer and a capping layer, pure Ge layers were formed under the condition shown in Figure 5 in which a single atomic layer of Ge was deposited on the Ge surface in every single flash light shot of 60 J/cm² at 260 °C. As a barrier layer, a Si_1Ge_1 atomic-layer superlattice was formed by depositing single atomic-layers of Si and Ge alternately at 275 °C, in which the SiH_4 and GeH_4 partial pressures were 500 Pa and the SiH_4 and GeH_4 exposure time were 20 min and 8 min, respectively. For the Ge single atomic-layer growth on the Si surface, GeH_4 exposure was stopped with the flash light shot of 60 J/cm² and the surface was finished by depositing a Ge atomic-layer for the growth of the QW and the capping layer. The diode structure was partially etched by using a CVD- SiO_2 mask and dilute $\text{HF-H}_2\text{O}_2\text{-H}_2\text{O}$ solution, and the etched surface was also passivated by CVD- SiO_2 . Metal electrodes were formed by a sputtered Al-1%Si alloy and no sintering was done to avoid Al spiking into the diode structure. In order to suppress an interdiffusion of Si and Ge at the hetero interface, all the fabrication processes during/after growing the diode structure were operated below 300 °C.

Figure 7: Schematic cross section of the resonant tunneling diode grown on Si(100). Inset shows the magnified view around resonant tunneling barriers.

Figure 8: Current–voltage characteristic at 10 K for the resonant tunneling diode by using self–limited atomic layer–by–layer growth control method. Arrows indicate the peak position.

Here, as a most simplified approximation, we assume that the valence–band discontinuity(ΔE_v) in $\text{Si}_1\text{Ge}_1/\text{Ge}$ is the same as the calculated value in alloyed $\text{Si}_{0.5}\text{Ge}_{0.5}/\text{Ge}$ [14]. Usually, tunneling probability of the light hole through the barriers is much larger than that of heavy hole. The bound state energy(E_{LH0}) was calculated to be 0.094 eV from Schrödinger equation using ΔE_v of 0.20 eV for light hole(effective mass of $0.043m_0$ (m_0 : electron mass in vacuum)) in Ge. Under uniform electric field approximation for the undoped region in a biased condition, resonant tunneling voltage(V_R) corresponding to E_{LH0} was estimated to be 0.69 V.

In the current–voltage characteristic shown in Figure 8, two peaks are clearly observed in the Ge / Si_1Ge_1 / Ge / Si_1Ge_1 / Ge system and they can be assigned to the resonant tunneling via the light–hole bound state in the Ge QW as calculated above. This suggests that the diode structure has an abrupt $\text{Si}_1\text{Ge}_1/\text{Ge}$ interface due to employing a low–temperature atomic layer–by–layer growth process. In order to clarify the relationship between crystal quality and device characteristics, further investigation is needed.

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References

- [1] Nishizawa J., Abe H. and Kurabayashi T., *J. Electrochem. Soc.* **132** (1985) 1197–1200.
- [2] Nishizawa J., Aoki K., Suzuki S. and Kikichi K., *J. Electrochem. Soc.* **137** (1990) 1898–1904.
- [3] Takahashi Y., Ishii H. and Fujinaga K., *J. Electrochem. Soc.* **136** (1989) 1826–1827.
- [4] Takahashi Y. and Urisu T., "Self Limiting Adsorption of SiCl_2H_2 and Its Application to the Layer-by-Layer Photochemical Process", Extended Abstracts of 1990 International Conference on Solid State Devices and Materials, Sendai, Japan, 1990 (The Japan Society of Applied Physics, Tokyo), pp.917–920.
- [5] Murota J., Sakuraba M. and Ono S., *Appl. Phys. Lett.* **62** (1993) 2353–2355.
- [6] Sakuraba M., Murota J. and Ono S., *J. Phys. IV France*, Colloque C3, **3** (1993) 449–456.
- [7] Sakuraba M., Murota J., Mikoshiba N. and Ono S., *J. Crystal Growth* **115** (1991) 79–82.
- [8] Murota J., Sakuraba M., Mikoshiba N. and Ono S., *J. Phys. IV France*, Colloque C1, **1** (1991) 803–808.
- [9] Kobayashi S., Cheng M. L., Kohlase A., Sato T., Murota J. and Mikoshiba N., *J. Crystal Growth* **99** (1990) 259–262.
- [10] Papagno L., Shen X. Y., Anderson J., Spagnolo G. S. and Lapeyre G. J., *Phys. Rev. B* **34** (1986) 7188–7191.
- [11] Gupta P., Colvin V. L. and George S. M., *Phys. Rev. B* **37** (1988) 8234–8243.
- [12] Ohtani N., Mokler S. M., Xie M. H., Zhang J. and Joyce B. A., *Surf. Sci.* **284** (1993) 305–314.
- [13] Goto K., Murota J. and Ono S., *Materials Science Forum* **117–118** (1993) 153–158.
- [14] Van de Walle C. G. and Martin R. M., *Phys. Rev. B* **34** (1986) 5621–5634.