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Si Atomic-Layer-Epitaxy Using Thermally-Cracked-Si_2H_6

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1. Introduction

Atomic-layer epitaxy (ALE) is an epitaxial film growth technique, with which, in its ideal form, a film can be epitaxially grown by monolayer-by-monolayer (ML) using a self-limited adsorption mechanism. With the development of Si/Ge quantum well devices, much attention has been focused on IV-element ALE to form Si/Ge-based atomic-layer structured devices. As for Si ALE, hydride molecules such as SiH_4, Si_2H_6, and Si_3H_8 have been intensively investigated for their potential advantage of being contamination-free [1-6]. However, their saturation coverages at room temperature are less than 1 ML and it is generally difficult to realize Si ALE with hydride molecules [5].

We have recently proposed a novel IV-element ALE method to use thermally-cracked hydride-molecules as precursors on the basis of the results of an investigation on the adsorption processes of thermally-cracked-Si_2H_6 on Ge(001) and Si(001) using RHEED (reflection high-energy electron diffraction) and AES (Auger electron spectroscopy) techniques [7]. In this paper, we report the recent results of Si ALE growth on Ge(001) with thermally-cracked-Si_2H_6 as a precursor. The results indicate that the Si/Ge interface is abrupt and Si ALE growth is obtained on both Si(001) and Ge(001). On the basis of the results, we further discuss the ALE mechanisms and its applicability to other systems.

2. Experimental

Thermally-cracked-Si_2H_6 adsorption experiments and Si ALE experiments with thermally-cracked-Si_2H_6 were carried out using a load-locked ultrahigh vacuum chamber equipped with RHEED and AES apparatuses. The base pressure of this chamber was < 5 x 10^{-10} Torr. 1-2.5 Ω-cm Ge(001) plates were used as substrates in the adsorption and ALE experiments. 5-7 Ω-cm Si(001) plates were also used as substrates in the adsorption experiments. Before insertion into the vacuum chamber, the Si(001) substrates were degreased, and the Ge(001) substrates were chemically cleaned. Clean double-domain Ge(001) 2x1 and Si(001) 2x1 surfaces were obtained after annealing. These cleaning procedures have been precisely described elsewhere [7]. To thermally crack Si_2H_6, we used an alumina tube with a tungsten spiral filament as a thermal cracking cell. The cracking temperature (T_C) was determined by the filament temperature, the value of which was controlled to be constant during cracking. Research-grade Si_2H_6 (99.999%) were used and the filament temperature was varied from 200 to 400 °C.

To analyze the adsorption mechanisms of the thermally-cracked-Si_2H_6 on Ge(001) and Si(001), the surface morphology after thermally-cracked-Si_2H_6 exposure were investigated by observing the RHEED patterns and Si adsorption coverage on Ge(001) were determined by AES analysis. In the AES analysis for Si adsorption coverage (θ_{Si}), Ge MVV (52 eV) and Ge LMM (1147 eV) Auger signals were detected and using these signal intensities, the corresponding Si coverage were analytically determined by utilizing the escape depth difference between Ge MVV and Ge LMM Auger electrons. For these escape depth values, we used those obtained from the relationship between Ge Auger intensities and Si coverage reported by Gossmann [8].

Si ALE growth were carried out by repeating a growth cycle consisting of (1) thermally-cracked-Si_2H_6 exposure (t_1), (2) evacuation (t_2), (3) annealing (t_3), and (4) cooling (t_4) processes. The heating process is incorporated to remove hydrogen from a thermally-cracked-Si_2H_6 exposed surface. Thermally-cracked-Si_2H_6 exposure were carried out after the surface was cooled down to under 80 °C.

3. Results and Discussion

Si Adsorption Coverage and RHEED Observations

When a Ge(001) surface was exposed to non-cracked Si_2H_6, the Si saturation coverage (θ_{Si}^{SAT}) determined by the AES analysis was around 0.55. This value is in good agreement with the previously reported value of ~0.5 the value of which is determined by both AES and STM (scanning tunneling microscopy) [9]. The Si saturation coverage has been interpreted to be submonolayer due to adsorption site occupation by dissociatively adsorbed hydrogen [9].

In Fig.1, we show the relationship between Si adsorption coverage and thermally-cracked-Si_2H_6 dose in langmuir (L). The cracking temperature (T_C) was 200 or 400 °C. The substrate surface temperature was nearly room temperature (RT). As shown in Fig.1, we have found that the Si adsorp-

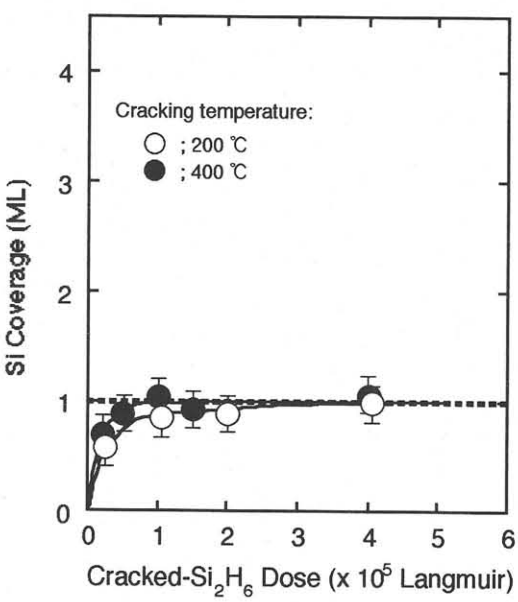

Fig.1 The relationship between Si adsorption coverage and thermally-cracked-Si_2H_6 dose obtained using a Ge(001) surface. The surface temperature is room temperature throughout the experiments

tion coverage approaches ~1 ML as the thermally-cracked-Si_2H_6 dose increases, and that in contrast to the case of non-cracked Si_2H_6 exposure on Ge(001) where θ_{Si}^{SAT} = ~0.55, the θ_{Si}^{SAT} value becomes ~1 ML. It is noted that the value for a non-cracked-Si_2H_6/Si(001) system is <~0.65 [6].

RHEED patterns of clean Ge(001) and Si(001) were double-domain 2x1. However, when both the surfaces were exposed to thermally-cracked-Si_2H_6, half-order spots were almost disappeared and the 2x1 periodicity changed to nearly 1x1 at a thermally-cracked-Si_2H_6 dose of 1~1.5 L. From these 1x1 surfaces, neither 3-dimensional pattern nor contaminant species were detected, indicating an atomically flat 1x1 surface.

Thus, at almost the same thermally-cracked-Si_2H_6 dose, the 2x1 periodicity of clean Ge(001) and Si(001) is changed to ~1x1 and the Si coverage using a Ge(001) surface saturates at ~1 ML. The first thermal dissociation reaction for gas phase Si_2H_6 has been reported as Si_2H_6 -> SiH_2 + SiH_4 [10, 11]. Since SiH_4 hardly reacts with Ge(001) and Si(001) at RT [12] and SiH_2 has reactive bonds, SiH_2 is expected to have much higher reactivity than SiH_4. Then, if SiH_2 covers the (001) surface, the surface periodicity becomes 1x1 and the corresponding Si coverage is 1 ML. Thus, this SiH_2-terminated surface model explains well the experimental results of this work, implying that SiH_2 may play an important role in the thermally-cracked-Si_2H_6/Ge(001) and thermally-cracked-Si_2H_6/Si(001) systems.

Si Atomic Layer Epitaxy (ALE)

Si ALE cycles were carried out with a thermally-cracked-Si_2H_6 dose of 1.5 x 10^5 L at T_C = 400 °C. The annealing temperature (T_A) and time (t_3) were varied from 300 to 500 °C and from 15 s to 1 min, respectively. A 500-°C 1-min anneal is enough to desorb hydrogen almost entirely [2]. The periods t_1, t_2, and t_4 in one ALE cycle were 15, 5, and 5 min, respectively.

In Fig.2, we show typical data of the relationship between the Si coverage and the number of ALE cycles. A Si coverage after the first cycle in each experiment is ~1 ML because in every first cycles, a thermally-cracked-Si_2H_6 exposure is carried out on the initial clean surface. When T_A = 400 °C, Si coverage increases by monolayer-by-monolayer and Si ALE is successfully realized. With T_A = 500 °C, however, Si coverage per cycle (G_R) after the second cycle was less than 1 ML/cycle. Since hydrogen is completely desorbed under the 500 °C anneal conditions, this submonolayer G_R is probably due to Si-Ge intermixing [9]. With T_A = 300 °C, the G_R again becomes ~0.55. Compared to the case of a H/Si(001) system [13], it is expected that some of monohydrides and dihydrides remain on the surface under the 300 °C anneal conditions and only some of monohydrides remain under the 400 °C anneal conditions. This analysis suggests that the thermally-decomposed species, which saturate the surface with 1-ML Si, reacts with monohydride and dose not react with dyhydride. Further precise experiments clarify these reaction mechanisms.

The result of Si ALE with T_A = 400 °C indicates that the Si coverage increases linearly by monolayer-by-monolayer, suggesting that abrupt Si-Ge interface junction is formed and Si ALE is also obtained on Si(001).

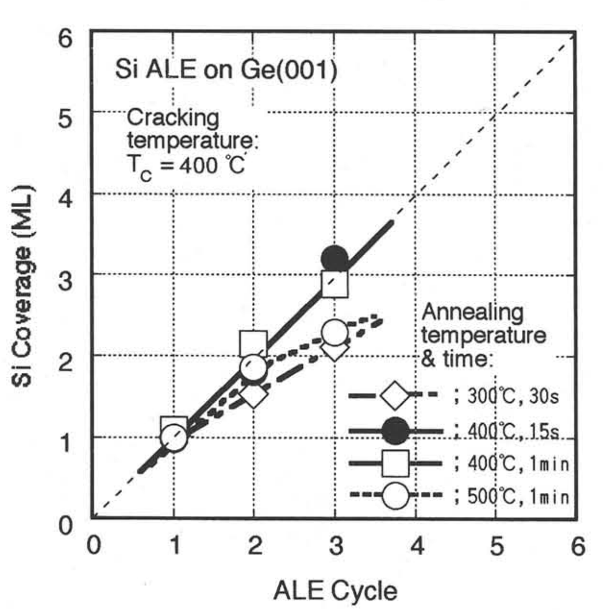

Fig. 2 The relationship between the Si coverage and the number of ALE cycle.

4. Conclusions

We first propose the use of thermally-cracked hydride-molecules as precursors for IV-element ALE. By the use of thermally-cracked-Si_2H_6, ~1-ML Si saturation coverage has been obtained on Ge(001) in contrast to the case of non-cracked-Si_2H_6 with which Si saturation coverages on Ge(001) and Si(001) are 0.45-0.65. With thermally-cracked-Si_2H_6 as a precursor, Si ALE has been successfully realized on Ge(001). The results also indicate that Si ALE is obtained on Si(001) and the Si/Ge interface is abrupt. With the cracking method, SiH_2 is suggested to play an important role in the saturation reaction. The proposed ALE method is expected to be also widely applied to other hydride molecules such as SiH_4, Si_3H_8, GeH_4, and Ge_2H_6.

References

1) see, e.g., Appl. Surf. Sci. **82/83** (1994).
2) Y. Suda, M. Ishida, M. Yamashita, and H. Ikeda: Appl. Surf. Sci. **82/83** (1994) 332.
3) Y. Suda, M. Shirahama, and M. Ishida: Trans. Mat. Res. Soc. Jpn. **19A** (1994) 149.
4) M. Ishida, M. Yamashita Y. Nagata and Y. Suda: Jpn. J. Appl. Phys. **35** (1996) 4011.
5) Y. Suda, M. Ishida, and M. Yamashita: J. Cryst. Growth **169** (1996) 672.
6) Y. Suda: J. Vac. Sci. Technol. A**15** (1997) 2463.
7) Y. Suda, Y. Misato, D. Shiratori, K. Oryu, and M. Yamashita: Appl. Surf. Sci. (1998) (in press).
8) H. J. Gossmann: *Ph. D. thesis, State Univ. of New York, Albany, 1984.*
9) R. Tsu, D. Lubben, T. R. Bramblett, J. E. Greene, D. -S. Lin and T. -C. Chiang: Surf. Sci. **280** (1993) 265.
10) K. F. Roenigk, K. F. Jensen and R. W. Carr: J. Phys. Chem. **91** (1987) 5732.
11) J. Dzarnoski, S. F. Rickborn, H. E. O'Neal and M. A. Ring: Organometallics, **1** (1982) 1217.
12) M. Sakuraba, J. Murota, T. Watanabe, Y. Sawada and S. Ono: Appl. Surf. Sci. **82/83** (1994) 354.
13) J. A. Schaefer, F. Stucki, J. A. Anderson, G. J. Lapeyre and W. Göpel: Surf. Sci. **140** (1984) 207.