

A Proposed Atomic-Layer-Deposition of Germanium on Si(100)

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A novel method has been proposed for monolayer deposition of Ge on the Si clean surface, where germanium tetrachloride and atomic hydrogen are exposed alternatively and repeatedly as a self-limiting precursor and a reactant for extraction reaction of surface-terminating Cl, respectively. It has been confirmed experimentally that Ge can be deposited uniformly with around one monolayer in thickness on the Si(100) surface.

1. Introduction

Atomic layer epitaxy (ALE)¹⁾ has the unique feature that the film can be grown in a self-limiting layer-by-layer manner, where spontaneous and undesired film growth is completely eliminated by the help of perfectly controlled adsorption of precursors and desorption of ligands from surface adsorbates. Thus the ALE produces an atomically flat grown-film having a precise thickness determined only by the number of execution cycle. Critical adjustments of growth parameters are not required owing to wide process margins, the so-called ALE window. Therefore, ALE of Si and Ge is expected a powerful technique for fabricating Si/Ge short-period superlattices in comparison with conventional method such as MBE or CVD where film growth is based on the adsorption of precursors to the free sites having been born by random desorption of surface-terminating ligands.

To fabricate the Si/Ge short-period superlattice by ALE, both the Ge hetero-ALE on the Si surface and Si hetero-ALE on the Ge surface should be established. The Ge hetero-ALE on the Si surface can be divided into two steps, which consist of one monolayer (ML) adsorption of Ge to the Si clean surface, and of successive Ge ALE on the newly formed Ge surface, i.e., Ge homo-ALE. This is because 1ML-adsorption conditions for Ge to the Si surface will differ from those to the Ge surface due to difference in chemical reactivity between the Si and Ge surfaces.

We have succeeded in the Ge homo-ALE by alternating exposures of atomic hydrogen, H, and dimethylgermane (CH₃)₂GeH₂, (DMG)²⁾. We have also reported the saturated coverage of Ge by exposing DMG to the Si(100) clean surface³⁾. 1ML-adsorption was achieved around 520°C, but its temperature window was very narrow since it was restricted by the undesirable adsorption of H to Si dangling bonds from precursors and by the undesirable desorption of surface-terminating methyl groups. Another problem was that undesirable Si-C bonds were born, that may be caused by transfer of methyl groups from DMG adsorbed to the Si surface, and/or mixing of the Ge/Si interface. Contamination-free 1ML-adsorption of Ge to Si is a remaining subject of investigation.

In this paper, we have proposed a new 1 ML-adsorption method named a "RPALD" method. Detailed

process steps and concept are presented together with experimental results.

2. Proposal of Repeated Precursor-Adsorption and Ligands-Desorption Method

Time sequence is shown in Fig.1 for a proposed RPALD method, i.e., repeated precursor-adsorption and ligands-desorption method. There are three important phases, i.e., a source gas exposure phase, an atomic H exposure phase, and a surface H desorption phase when the sample is heated up in vacuum. These phases are repeated by turns for about 15 cycles. And we have used germanium tetrachloride (GTC: GeCl₄) as the Ge source gas.

Schematic view is shown in Fig.2 for surface conditions in several representative scenes in Fig.1. In the first GTC exposure phase, GTC is adsorbed dissociatively to the Si clean surface, resulting in GeCl_x, elemental Ge and SiCl_x surface species^{4,5)} with the saturated Ge coverage of about 1/3ML as shown in (a). GTC is not adsorbed excessively, not only to SiCl_x and GeCl_x by adsorbate inhibition⁶⁾ due to the surface-terminating Cl, but also to elemental Ge by the selective adsorption effects⁶⁾ of GTC. In the successive atomic H exposure phase, surface-terminating Cl is completely removed by the desirable extraction reaction of atomic H⁷⁾. Substrate temperature should be kept sufficiently low in these two phases in order to suppress Cl desorption from the surface. Thus, after extraction of Cl, H will be adsorbed to Si and Ge dangling bonds, resulting in the H-terminated surface as shown in (b). During the next H desorption phase of high substrate temperature, H is thermally desorbed from the surface^{8,9)}, and the clean surface is recovered as shown in (c). Density of Si dangling bonds is, however, decreased to about two-third of its initial value since Ge having been adsorbed during the first GTC exposure phase still remains on the surface. The next GTC exposure phase is then started, and due to the selective adsorption phenomena of GTC, the Ge coverage is increased to 1/3+(1-1/3)×(1/3) ML as shown in (d). By continuing these three phases cyclically, the Ge coverage will be increased and saturated at 1ML for large cycle number n, having an asymptotic form of 1-(2/3)ⁿ. The Ge coverage will be more than 0.99ML for n=15.

In order to realized the above mentioned surface

condition in each phase, the following requirements should be satisfied:

In the GTC exposure phase

- (1) No etching of Si and Ge surfaces by GTC
- (2) No-adsorption of GTC to elemental Ge as well as to Cl-terminated Si and Ge
- (3) Dissociative adsorption of GTC to Si
- (4) No-desorption of surface-terminating Cl

In the H exposure phase

- (5) No etching of Si and Ge surfaces by atomic H
- (6) Complete reduction of Cl from surface Si-Cl and Ge-Cl adsorbates by atomic H

In the H desorption phase

- (7) Complete desorption of surface-terminating H

3. Experimental

Experiments were carried out using an ultra-high vacuum ALE system whose details were described elsewhere²⁾. The sample was of single crystal of Si(100) wafer. After growing buffer layer of 30nm in thickness, the sample was heated in high vacuum to remove surface H, and then experiments were started. The source gas and atomic H dosing procedures were the same as the previously described ones²⁾. A standard set of experimental parameters is shown in Table 1.

The Ge coverage was evaluated from the photoelectron intensity ratio I_G/I_S between Si2p and Ge3d core level spectra obtained by XPS (X-ray photoelectron spectroscopy). The ratio was calibrated by the results of the 1/2ML Ge-adsorbed Si surface formed by DMG exposure at room temperature^{3,10)}. Inelastic mean free path of photoelectrons was assumed equal to their escape depth¹¹⁾.

4. Results and Discussion

Many workers have reported that the above mentioned requirements (6) and (7) are satisfied. We have confirmed by preliminary experiments that requirements from (1) to (5) are also satisfied. Based on these results, IML-adsorption has been investigated.

Figure 3 shows dependence of the ratio I_G/I_S on cycle number. The Ge coverage was increased with n , and saturated at about 1.1ML, a little thicker than the desirable value. The most possible origin of this "excess" adsorption is in the ambiguity of the photoelectron escape depth. Other possible origins will be mixing of Ge/Si interface, different effects to photoelectron attenuation of surface methyl groups on Si and Ge, and so on.

A solid curve in the figure is the theoretically predicted ratio under the assumption that Ge is adsorbed to one-third of Si dangling bonds by a GTC exposure. Measured results show clear saturation characteristics as predicted but with slower speed. This seems to be caused by the insufficient desorption of surface H during the H desorption phase as shown in Fig. 4, where the ratio I_G/I_S is plotted as a function of the H desorption duration, for execution cycle number of 15. The Ge surface coverage was increased by elongating H desorption phase and saturated at 1.1ML. H desorption duration used as a standard value was not satisfactory for complete H

desorption from the surface. This seems the dominant reason of the difference between experimental and theoretical results appeared in Fig. 3.

Figure 5 shows the intensity ratio I_G/I_S as a function of the take-off angle by angle-resolved XPS. Data are on an ideal curve of uniform IML-adsorption of Ge on Si(100) surface shown by a solid curve.

5. Conclusion

We have proposed a RPALD method for the formation of the IML Ge layer on the Si surface using cyclic exposures of GTC and atomic H, and temperature-programmed surface H desorption. Ideal IML adsorption of Ge has been confirmed experimentally for the Si(100) surface. We expect that by following the Ge-ALE to this IML Ge formation scheme, Ge layer can be grown epitaxially in layer-by-layer manner on the Si surface with atomically abrupt and flat interface.

References

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Table 1 Experimental conditions

Substrate	Si(100)
GTC pressure	30mTorr
GTC exposure time (t_G)	3s
H ₂ flow rate	0.5sccm
Filament temperature	1900 °C
Atomic H exposure time (t_H)	10s
H desorption time (t_h)	15s
T_{sub} in GTC and H exposure phases (T_1)	300 °C
T_{sub} at H desorption phase (T_h)	500 °C

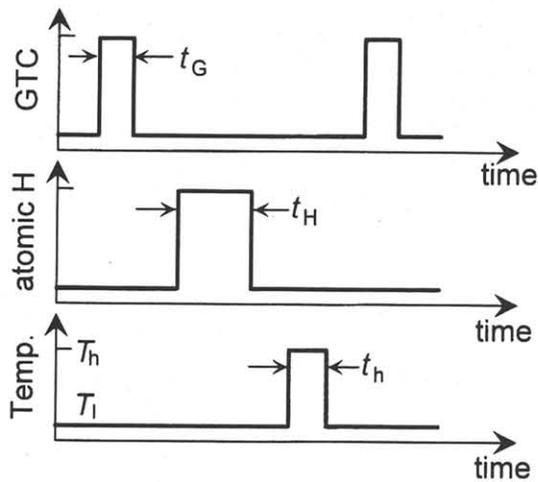


Fig. 1. Proposed time sequence

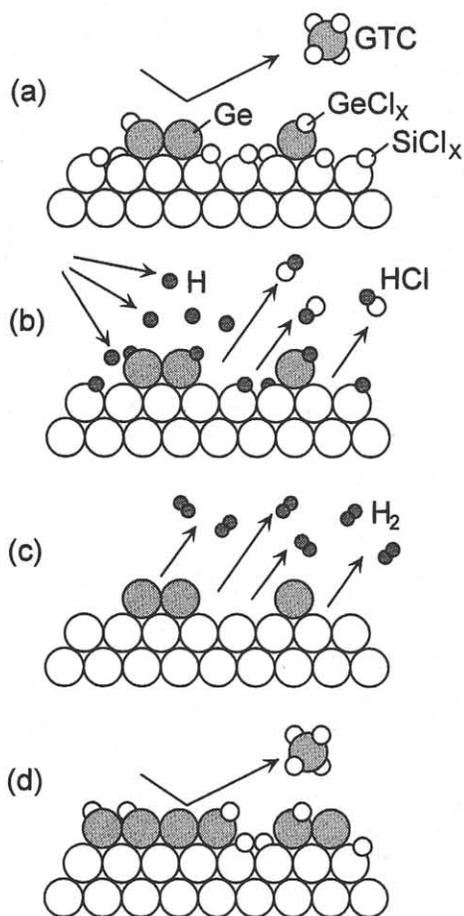


Fig. 2. Schematics of surface condition

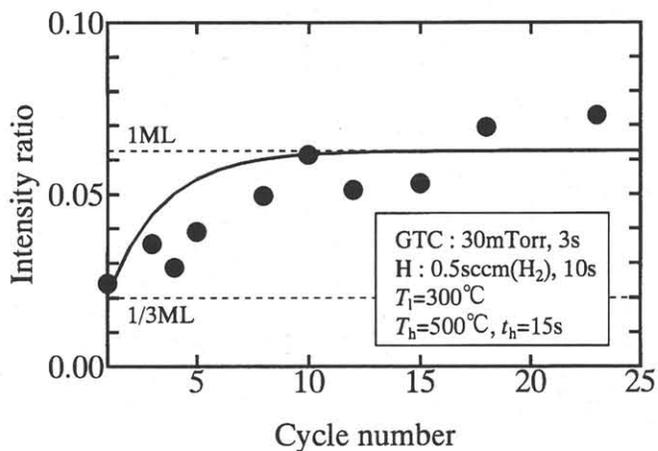


Fig. 3. Growth rate as a function of cycle number

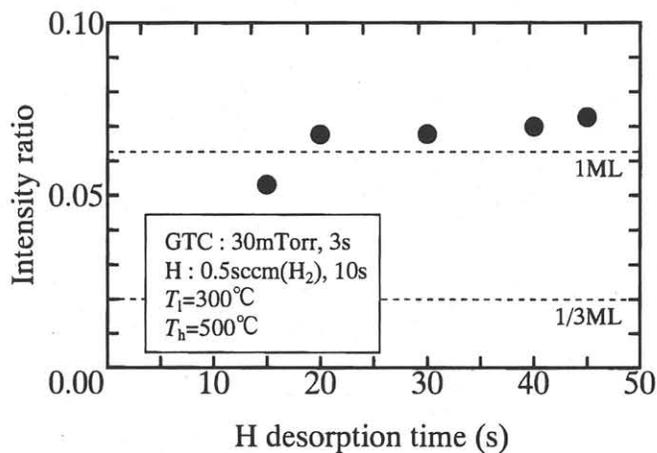


Fig. 4. Growth rate as a function of the H desorption duration

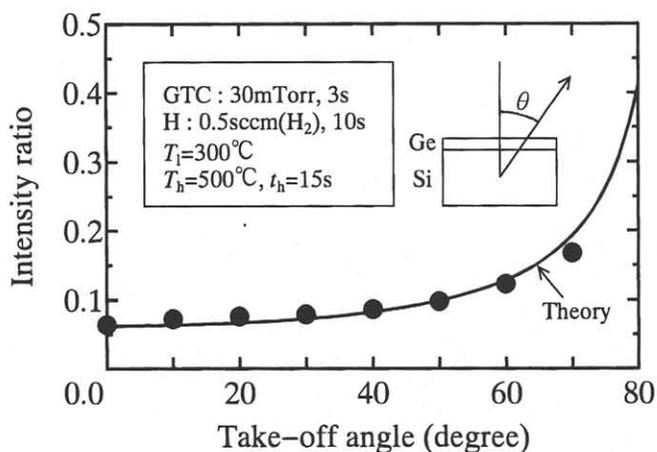


Fig. 5. XPS intensity ratio as a function of take-off angle