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Self Limiting Adsorption of $SiCl_2H_2$ and Its Application to the Layer-by-Layer Photochemical Process

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Adsorption of $SiCl_2H_2$ on the Ge(100) clean surface is investigated by x-ray photoelectron spectroscopy and thermal desorption spectrum measurement. It is concluded that the adsorption is limited by the monolayer at temperatures less than 350° C. An area selective layer-by-layer epitaxial growth of Si on Ge(100) surface is obtained by the sequential processes of the self-limiting adsorption of $SiCl_2H_2$ and the irradiation of synchrotron radiation.

1. INTRODUCTION

Self-limiting adsorption is a key process in atomic layer epitaxy (ALE), which is an attractive technique for the semiconductor film growth with very fine thickness control. Most current ALE investigations have concentrated on II-VI and III-V compound semiconductor materials[1-2], while only a small number of researches have been reported on elemental materials such as Si and Ge. Concerning Ge, ALE processes have succeeded using self-limiting adsorption of $GeEt_2H_2$ ($Et=C_2H_5$) or $GeMe_2H_2$ ($Me=CH_3$)[3-5]. On the other hand, ALE of Si has only been studied theoretically[6] and no experimental research on Si with either ALE or self-limiting adsorption phenomena has been presented, despite the fact that Si is the host material in conventional LSI.

In this paper, the self-limiting adsorption of $SiCl_2H_2$ and its potential application to Si ALE are experimentally investigated. The first step to realize ALE is to find a suitable molecule containing Si atoms which has a self-limiting adsorption property. The second step is to find a method, which breaks the self-limiting property to enable the adsorption of the second layer. It has been found that $SiCl_2H_2$ shows a self-limiting adsorption on a Ge(100) substrate and also that the self-limiting property is broken by synchrotron radiation (SR). Area selective deposition by layer-by-layer photochemical process is also demonstrated.

2. EXPERIMENT

Self-limiting adsorption characteristics were investigated by using a substrate of 30-nm-thick Ge film grown epitaxially on an Si (100) wafer at 430° C by the GeH_4 CVD process[7]. The epitaxial growth of Ge was confirmed by RHEED patterns. The substrates were exposed to $SiCl_2H_2$ gas in a turbomolecular-pumped high vacuum reactor with a base pressure of about 10^{-7} Pa just after the Ge epitaxial growth. Then, the sample was transferred to an evaluation chamber, where the sample surface was analyzed by x-ray photoelectron spectroscopy

(XPS) using Al Kα x-rays (1486.6 eV) in a high vacuum of 10^{-8} Pa. Si_{2p} photoelectron intensity normalized by Ge_{3d} was monitored to evaluate the amount of the adsorption. The escape depth (2-3 nm) of the Ge_{3d} photoelectron is much longer than one atomic layer thickness.

To investigate the chemical species adsorbed on the substrate surface, the temperature-programmed desorption (TPD) spectrum[3] was measured using a high vacuum quartz reactor[3,8], in which the sample is placed on the quartz boat and heated by infrared lamp. The base pressure of the reactor was 10^{-6} Pa. Adsorption of $SiCl_2H_2$ on the quartz surface was not observed by TPD. A quadrupole mass spectrometer was used to detect molecules which desorb from the sample surface.

Experiments on the layer-by-layer photochemical process were carried out using SR experimental systems[9] of beam line 1C in the Photon Factory at the Institute of High Energy Physics, Tsukuba. The base pressure of the reaction chamber was $5x10^{-8}$ Pa. The white beam, ranging from 1 nm to 100 nm with a peak of 3 nm was used. The total power of the irradiation beam was about 2 W. The beam shape on the sample surface was an ellipse with 2 mm and 6 mm diameters.

3. RESULTS AND DISCUSSION

Figure 1 shows the observed relation between the XPS signal intensity ratio of Si_{2p}/Ge_{3d} and the gas exposure after exposing the substrate to $SiCl_2H_2$ gas at a substrate temperature of 120° C. Here, the amount of the gas adsorption saturated at an exposures of about 10^5 L ($1L=10^{-6}$ torr sec) or more means that self-limiting adsorption occurs.

Figure 2 shows the XPS signal intensity ratio of Si_{2p}/Ge_{3d} after gas exposure at various substrate temperatures. In this

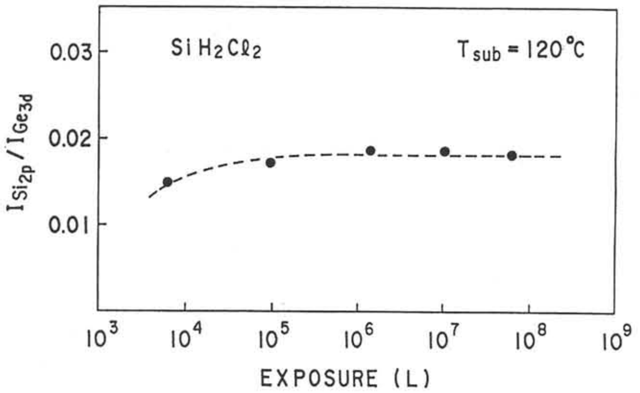

Fig. 1 Dependences of XPS intensity ratio between Si_{2p} and Ge_{3d} on exposure to $SiCl_2H_2$ gas on the Ge (100) surface. Substrate temperature is 120° C.

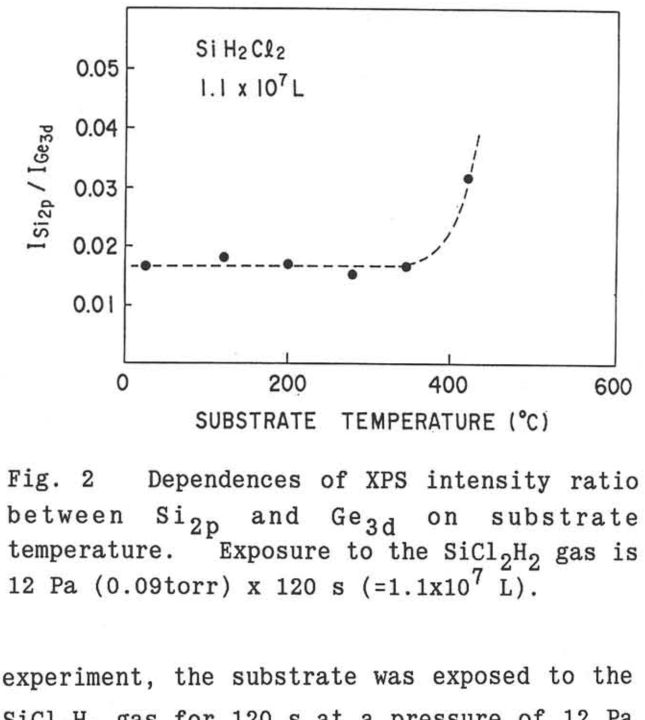

Fig. 2 Dependences of XPS intensity ratio between Si_{2p} and Ge_{3d} on substrate temperature. Exposure to the $SiCl_2H_2$ gas is 12 Pa (0.09torr) x 120 s ($=1.1x10^7$ L).

experiment, the substrate was exposed to the $SiCl_2H_2$ gas for 120 s at a pressure of 12 Pa ($1.1x10^7$ L). It is known that self-limiting adsorption is preserved up to about 350° C and that the amount of surface Si increases at temperatures above that. Figure 3 shows the typical TPD spectra measured for the Ge (100) surface after exposure to $SiCl_2H_2$ gas at $2x10^6$ L at 120° C where mass number 35 (Cl) was monitored. The rate of substrate temperature increase was 30° C/min. The broken line indicates the TPD spectrum observed for the Si substrate

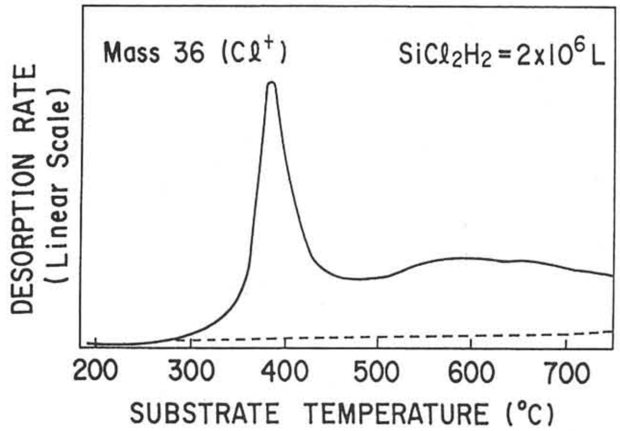

Fig. 3 Observed thermal desorption spectra of Cl atoms from the Ge (100) surface exposed to $SiCl_2H_2$ gas. Exposure is $2x10^6$ L. Rate of substrate temperature increase is 30° C/min. Broken line indicates the TPD spectrum observed for the Si substrate covered with thermal SiO_2 film.

covered with thermal SiO_2 film. This indicates that $SiCl_2H_2$ does not adsorb on the SiO_2 surface and that desorption from the substrate holder and/or the reactor wall is negligible. From these figures, it is concluded that the self-limiting mechanism operates in a temperature range of about 350° C or less. The species observed in the thermal desorption is Cl. The dissociation energy for $SiCl_2H_2 \rightarrow SiCl_2+H_2$ (33 kJ/mol) is much smaller than that of $SiCl_2H_2 \rightarrow SiH_2+Cl_2$ (423 kJ/mol)[6]. Therefore, the reaction of self-limiting adsorption should be expressed by

$$SiCl_2H_2 + [\text{ Ge substrate }] \rightarrow [\text{ Ge substrate }]{>}SiCl_2 + H_2.$$

The self-limiting mechanism is maintained by the Cl atoms of adsorbed $>SiCl_2$. The desorption of Cl atoms at substrate temperatures above 350° C (Fig. 3) and the rapid increase of the Si atom deposition at about 400° C (Fig. 2) indicate that the self-limiting mechanism is broken by the thermal desorption of Cl. However, this does not mean that Si ALE can be attained by $SiCl_2H_2$ adsorption and substrate temperature control as is the case with $GeEt_2H_2$[3,5]. The TPD spectrum shown in Fig. 3 indicates that Cl atoms can not be desorbed completely by only increasing the temperature. Furthermore, atom mixing at the Si/Ge interface was observed at substrate temperatures above 400° C. Thus, it is concluded that the layer-by-layer process is difficult to achieve by the thermal process only.

To overcome this problem, the desorption of Cl atoms by the photochemical process induced by VUV photon irradiation is considered. The absorption spectrum measured preliminarily shows that $SiCl_2H_2$ can be excited efficiently by photons with a wavelength shorter than 150 nm. Thus, SR is a suitable light source for the excitation of this molecule. Figure 4 shows the AES spectra from the surface of Ge substrate after five cycles of the layer-by-layer process at 300° C. Each cycle consisted of four procedures: (1) $SiCl_2H_2$ gas exposure of $1.1x10^7$ L (8 Pa, 180 min) without SR irradiation, (2) 1 min evacuation pumping to less than 10^{-5} Pa, (3) 1 min SR irradiation, and (4) 4 min exposure to 4 Pa H_2 gas under SR irradiation. The last procedure was added for the complete elimination of the desorbed Cl atoms, but its effectiveness was not investigated. Spectra (b) and (c) correspond to the irradiated and nonirradiated areas, respectively. It is known that four to five times as many Si atoms are deposited on the irradiated area than on the nonirradiated area. The Si KLL AES signal intensity in the spectrum (b) corresponds to three to five atomic layers. The RHEED pattern for both irradiated and nonirradiated areas after the deposition was the same 2x1 reconstructed pattern observed just after the cleaning of the Ge substrate.

These results indicate that area selective layer-by-layer Si epitaxial growth is realized by a combination of the self-limiting adsorption of $SiCl_2H_2$ molecules and the breaking of the self-limiting mechanism by SR irradiation.

4. CONCLUSIONS

It has been found that the adsorption of $SiCl_2H_2$ on the Ge(100) surface is self-limiting at temperatures less than 350°C, where Cl atoms of the adsorbed $>SiCl_2$ hinder successive adsorption. Surface Cl atoms can be desorbed by substrate temperature increase. However, atom mixing at the Si/Ge interface occurs at above 400°C. The area selective layer-by-layer epitaxial growth of Si on the Ge(100) surface has been realized by the sequential processes of the self-limiting adsorption of $SiCl_2H_2$ and SR irradiation.

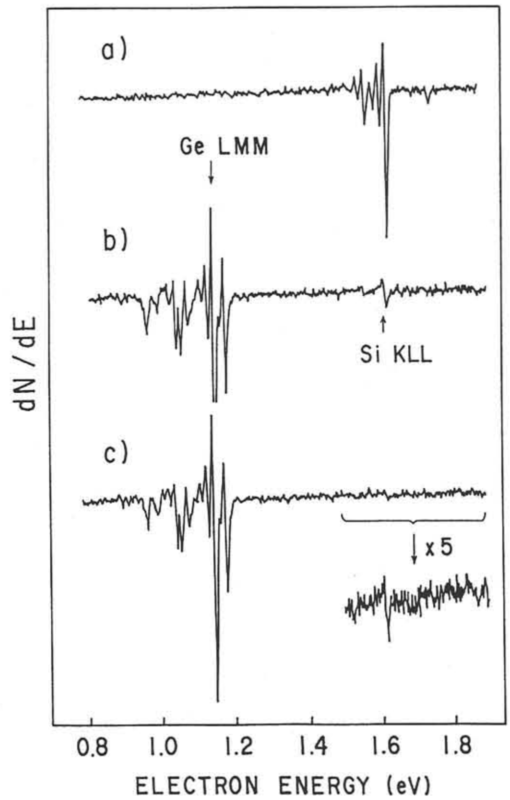

Fig. 4 Observed AES spectra for (a) bulk Si, (b) the SR irradiated area, and (c) the nonirradiated area on the Ge surface after five cycles of the layer-by-layer process.

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