Low-temperature epitaxial growth of in-situ B-doped Si$_{1-x}$Ge$_x$ films

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Abstract.—We report in-situ boron doping of Si$_{1-x}$Ge$_x$ films epitaxially grown on Si(100) by low-pressure chemical vapour deposition (LPCVD) process. The experiments are performed in an ultraclean hot-wall system using ultra-pure SiH$_4$-GeH$_4$-H$_2$-B$_2$H$_6$ gas mixtures. The incorporation rate of B was proportional to the B$_2$H$_6$ partial pressure and was larger for Ge-rich films. It was proposed that the increase in B incorporation rate with increasing Ge fraction was caused by the larger surface adsorption rate of B-hydride on Ge atoms than on Si atoms. Since the incorporation rate of B increased with exposure time of B$_2$H$_6$ during Si$_{1-x}$Ge$_x$ deposition at early stage, it was suggested that B doping was limited by the B-hydride adsorption rate. Hall measurements showed that carrier concentration was equal to B concentration in the range 3x10$^{17}$-2x10$^{20}$ cm$^{-3}$, regardless of the Ge fraction, and Hall mobility passed through a minimum value for Si$_{0.75}$Ge$_{0.25}$ films regardless of the film thickness.

1. - Introduction.

The epitaxial growth of in-situ doped Si$_{1-x}$Ge$_x$ films on Si at low-temperatures has become increasingly important for the fabrication of novel heterodevices [1,2]. Low-temperature LPCVD allows epitaxial growth of high quality Si$_{1-x}$Ge$_x$ layers [3-6] of various thicknesses and doping concentrations, e.g. abrupt steps in the doping profile, which is a key point for realizing devices with good performance. However, little is known about in-situ doping in heteroepitaxy of Si$_{1-x}$Ge$_x$ films on Si [7,8] and electrical characteristics of doped Si$_{1-x}$Ge$_x$ epitaxial films [9].

In the present work, in-situ B doping of Si$_{1-x}$Ge$_x$ films epitaxially grown on Si at 550°C and the relationship among resistivity, Hall mobility and carrier concentration for various Ge fractions in B-doped Si$_{1-x}$Ge$_x$ film have been investigated.

2. - Experimental.

The epitaxial growth of in-situ B-doped Si$_{1-x}$Ge$_x$ films was carried out at 550 °C in a SiH$_4$-GeH$_4$-H$_2$-B$_2$H$_6$ gas mixture using an ultraclean hot-wall LPCVD system [10] (Figure 1). The LPCVD system was made ultrahigh vacuum compatible with gate valves and a turbo molecular pump system. The optimized deposition process sequence for high quality Si$_{1-x}$Ge$_x$ heteroepitaxial growth on Si using this system have been described in detail elsewhere [4-6]. In the present experiment, the deposition temperature was 550°C except for B-doped Ge deposition at 350°C and B-doped Si deposition at 650°C. The total deposition pressure was about 30 Pa, and the partial

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Pressures of SiH₄, GeH₄, and B₂H₆ were in the range 1.5-11.2, 5.0x10⁻²-6.0, and 1.25x10⁻⁹-1.25x10⁻⁶ Pa, respectively. The film thicknesses range from 14 to 500 nm. The substrates used were n-type Si wafers of 3-5 ohm-cm with mirror polished (100) surfaces. Before loading the wafers into the transfer chamber, they were cleaned in several cycles in a 4:1 solution of H₂SO₄ and H₂O₂, high-purity DI water, and 1% HF with the final rinse in DI water.

The Ge fraction x was estimated from the lattice constant of a thick relaxed Si₁₋ₓGeₓ film deposited under the same conditions. The lattice parameter was determined by x-ray diffraction. The B concentration in Si₁₋ₓGeₓ films was determined by secondary ion mass spectroscopy. The film thickness was measured by using a Tencor Alpha Step. The surface structure was evaluated by electron diffraction. To measure the carrier concentration and Hall mobility in Si₁₋ₓGeₓ films, a clover-leaf area of Si₁₋ₓGeₓ film on Si substrate was defined by photolithography and chemical etch, and the sheet resistivity and Hall coefficient were measured by the van der Pauw method at room temperature.

![Diagram of the ultraclean hot-wall LPCVD system.](image)

Fig. 1.-Schematic diagram of the ultraclean hot-wall LPCVD system.

### Results and Discussion

Figure 2 shows the dependence of B concentration in Si₁₋ₓGeₓ films on the B₂H₆ partial pressure. The B concentration is linear with B₂H₆ partial pressure. Deposition rate and Ge fraction x of Si₁₋ₓGeₓ films scarcely depend on the B₂H₆ partial pressure.

![Graph showing B₂H₆ partial pressure dependence of B concentration in Si₁₋ₓGeₓ films.](image)  

![Graph showing B₂H₆ partial pressure dependence of deposition rate of Si₁₋ₓGeₓ films.](image)
pressure as shown in Figures 3 and 4. From Figures 2 and 3, the dependence of B incorporation rate, given by the product of the B concentration $C_B$ and the deposition rate $R$, on the $B_2H_6$ partial pressure is obtained as shown in Figure 5. The incorporation rate of B is linear with the $B_2H_6$ partial pressure, and the slope increases with increasing the $GeH_4/SiH_4$ partial pressure ratio. This means that the incorporation rate of B increases with increasing Ge fraction since the Ge fraction is determined by the $GeH_4/SiH_4$ partial pressure ratio [11]. Therefore, it is suggested that the incorporation of B into $Si_{1-x}Ge_x$ films is not limited by the mass-transport of B-hydride in the gas phase, but is controlled by the surface reactions. Assuming that $B_2H_6$ molecules are decomposed completely into BH$_3$ in the gas phase [12], it is considered that BH$_3$ is adsorbed at adsorption sites on the deposited $Si_{1-x}Ge_x$ surface. It was reported that, for $Si_{1-x}Ge_x$ deposition in the $SiH_4-GeH_4$ gas mixture, $SiH_4$ is dominantly adsorbed at adsorption sites based on a Langmuir adsorption isotherm under the same deposition conditions as in the present experiments [11]. However, at the $GeH_4/SiH_4$ partial pressure ratio of 1/30, the incorporation rate of B into $Si_{1-x}Ge_x$ films was independent of the $SiH_4$ partial pressure in the range 3.0-11.2Pa, although Si-hydride surface adsorption increases.

![Fig.4.-B$_2$H$_6$ partial pressure dependence of Ge fraction in $Si_{1-x}Ge_x$ films.](image)

![Fig.5.-B$_2$H$_6$ partial pressure dependence of $C_B \times R$.](image)

![Fig.6.-Deposition time dependence of B concentration in $Si_{0.75}Ge_{0.25}$ films.](image)

![Fig.7.-Dependence of B concentration in $Si_{0.75}Ge_{0.25}$ films on the $B_2H_6$ exposure time before film deposition.](image)
with increasing the SiH₄ partial pressure. Therefore, it is proposed that B-hydride surface adsorption occurs regardless of Si-hydride surface adsorption, and as a result, the B concentration in Si₁₋ₓGeₓ films is determined by the balance between the surface adsorption rate of B-hydride and the deposition rate. Based on this model, it is concluded that the increase in B incorporation rate with increasing Ge fraction is caused by the larger surface adsorption rate of B-hydride on Ge atoms than on Si atoms.

The deposition time dependence of B concentration in Si₀.₇₅Ge₀.₂₅ films is shown in Figure 6. B concentration is lower at the early stage of the growth (thickness ≈ 14-46nm). It was confirmed that Ge fraction and deposition rate scarcely depend on film thickness [6]. By an increase in B₂H₆ exposure time before Si₀.₇₅Ge₀.₂₅ deposition, B concentration at early stage increases and tends to become nearly equal to that in the thicker film as shown in Figure 7. Therefore, it is suggested that B doping is limited by B-hydride adsorption rate at early stage. In other words, the time for reaching the surface adsorption equilibrium of B-hydride is longer than that of Si- and Ge-hydride.

The relationship between carrier and B concentrations in the deposited Si₁₋ₓGeₓ films is shown in Figure 8. It is found that carrier concentration is equal to B

![Graph showing the relationship between B concentration and carrier concentration in B-doped Si₁₋ₓGeₓ films.](image1)

Fig. 8. Relationship between carrier and B concentrations in B-doped Si₁₋ₓGeₓ films.

![Graph showing the relationship between resistivity and carrier concentration in B-doped Si₁₋ₓGeₓ films.](image2)

Fig. 9. Relationship between resistivity and carrier concentration in B-doped Si₁₋ₓGeₓ films. Film thicknesses range from 200 to 500nm.
concentration in the range $3 \times 10^{17} - 2 \times 10^{20}$ cm$^{-3}$, regardless of the Ge fraction. In the present experiments, electron diffraction measurements showed that B doped Si$_{1-x}$Ge$_x$ films obtained were epitaxial. The relationship among resistivity, Hall mobility and carrier concentration for various Ge fraction is shown in Figures 9 and 10. Hall mobility exhibits a minimum value for Si$_{0.7}$Ge$_{0.3}$ films in B concentration below $10^{20}$ cm$^{-3}$, whose value is lower than that observed in Si, and then increases with Ge fraction. For Ge fraction of 0.25, it is considered that Hall mobility is influenced by alloy scattering [9]. It should be noted that the Hall mobility in the present Ge and Si films is nearly equal to that in bulk [13,14] as shown in Figure 10. The relationship among Hall mobility, carrier concentration and Si$_{0.75}$Ge$_{0.25}$ film thickness is shown in Figure 11. With increasing the thickness, Hall mobility decreases and carrier concentration increases. These data can be plotted on the line for Si$_{0.75}$Ge$_{0.25}$ films shown in Figure 10. It was confirmed that the current flow into substrate can be neglected in the present Hall measure-
ments based on the result that sheet resistivity and Hall coefficient of 14nm-thick Si$_{0.75}$Ge$_{0.25}$ film shown in Figure 11 were independent of current in the range $10^{-6}$ - $2.5\times10^{-5}$ A. From these results, Hall mobility would scarcely depend on the film thickness range 14-500nm if all the films of different thickness had the same carrier concentration. In other words, the mobility of the strained Si$_{0.75}$Ge$_{0.25}$ film is nearly equal to that of the unstrained one, since it is well known that the critical thickness for Si$_{0.75}$Ge$_{0.25}$ film grown on Si(100) is about 100nm [15].

4.-Conclusions.

B-doped Si$_{1-x}$Ge$_x$ films have been epitaxially grown on Si(100) at 550°C by LPCVD. The incorporation rate of B increases proportionally with increasing B$_2$H$_6$ partial pressure and is larger on the deposited Si$_{1-x}$Ge$_x$ film with higher Ge fraction x. It is proposed that the increase of B incorporation rate with increasing Ge fraction is caused by a larger surface adsorption rate of B-hydride on Ge atoms than on Si atoms. Since the incorporation rate of B increased with exposure time of B$_2$H$_6$ during Si$_{1-x}$Ge$_x$ deposition at early stage, it is suggested that B doping is limited by B-hydride adsorption rate. In other words, time for reaching the surface adsorption equilibrium of B-hydride is longer than that of Si- and Ge-hydride.

Hall measurements show that the carrier concentration is nearly equal to B concentration in the range $3\times10^{17}$ - $2\times10^{20}$ cm$^{-3}$, regardless of the Ge fraction, and Hall mobility has a minimum value for Si$_{0.75}$Ge$_{0.25}$ film, and the mobility of the strained Si$_{0.75}$Ge$_{0.25}$ film is nearly equal to that of the unstrained one.

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