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J. Murota, F. Honma, T. Yoshida, K. Goto, T. Maeda, et al.. Low-temperature epitaxial growth of in-situ B-doped Si_{1-x}Gex films. Journal de Physique IV Proceedings, 1993, 03 (C3), pp.C3-427-C3-432. 10.1051/jp4:1993359 . jpa-00251416

HAL Id: jpa-00251416

<https://hal.science/jpa-00251416>

Submitted on 1 Jan 1993

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

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Abstract.—We report in-situ boron doping of $\text{Si}_{1-x}\text{Ge}_x$ 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 $\text{SiH}_4\text{-GeH}_4\text{-H}_2\text{-B}_2\text{H}_6$ gas mixtures. The incorporation rate of B was proportional to the B_2H_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_2H_6 during $\text{Si}_{1-x}\text{Ge}_x$ 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 3×10^{17} – $2 \times 10^{20} \text{ cm}^{-3}$, regardless of the Ge fraction, and Hall mobility passed through a minimum value for $\text{Si}_{0.75}\text{Ge}_{0.25}$ films regardless of the film thickness.

1.—Introduction.

The epitaxial growth of in-situ doped $\text{Si}_{1-x}\text{Ge}_x$ 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 $\text{Si}_{1-x}\text{Ge}_x$ 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 $\text{Si}_{1-x}\text{Ge}_x$ films on Si [7,8] and electrical characteristics of doped $\text{Si}_{1-x}\text{Ge}_x$ epitaxial films [9].

In the present work, in-situ B doping of $\text{Si}_{1-x}\text{Ge}_x$ 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 $\text{Si}_{1-x}\text{Ge}_x$ film have been investigated.

2.—Experimental.

The epitaxial growth of in-situ B-doped $\text{Si}_{1-x}\text{Ge}_x$ films was carried out at 550 °C in a $\text{SiH}_4\text{-GeH}_4\text{-H}_2\text{-B}_2\text{H}_6$ 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 $\text{Si}_{1-x}\text{Ge}_x$ 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 SiH_4 , GeH_4 and B_2H_6 were in the range 1.5–11.2, 5.0×10^{-2} –6.0, and 1.25×10^{-5} – 1.25×10^{-3} 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 H_2SO_4 and H_2O_2 , 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 $\text{Si}_{1-x}\text{Ge}_x$ film deposited under the same conditions. The lattice parameter was determined by x-ray diffraction. The B concentration in $\text{Si}_{1-x}\text{Ge}_x$ 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 $\text{Si}_{1-x}\text{Ge}_x$ films, a clover-leaf area of $\text{Si}_{1-x}\text{Ge}_x$ 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.

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

3.-Results and discussion

Figure 2 shows the dependence of B concentration in $\text{Si}_{1-x}\text{Ge}_x$ films on the B_2H_6 partial pressure. The B concentration is linear with B_2H_6 partial pressure. Deposition rate and Ge fraction x of $\text{Si}_{1-x}\text{Ge}_x$ films scarcely depend on the B_2H_6 partial

Fig.2.- B_2H_6 partial pressure dependence of B concentration in $\text{Si}_{1-x}\text{Ge}_x$ films.

Fig.3.- B_2H_6 partial pressure dependence of deposition rate of $\text{Si}_{1-x}\text{Ge}_x$ films.

Fig. 4. - B_2H_6 partial pressure dependence of Ge fraction in $Si_{1-x}Ge_x$ films.

Fig. 5. - B_2H_6 partial pressure dependence of $C_B \times R$.

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 3.0-11.2 Pa, although Si-hydride surface adsorption increases

Fig. 6. - Deposition time dependence of B concentration in $Si_{0.75}Ge_{0.25}$ films.

Fig. 7. - Dependence of B concentration in $Si_{0.75}Ge_{0.25}$ films on the B_2H_6 exposure time before film deposition.

with increasing the SiH_4 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 $\text{Si}_{1-x}\text{Ge}_x$ 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 $\text{Si}_{0.75}\text{Ge}_{0.25}$ films is shown in Figure 6. B concentration is lower at the early stage of the growth (thickness $\approx 14\text{-}46\text{nm}$). It was confirmed that Ge fraction and deposition rate scarcely depend on film thickness [6]. By an increase in B_2H_6 exposure time before $\text{Si}_{0.75}\text{Ge}_{0.25}$ 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 $\text{Si}_{1-x}\text{Ge}_x$ films is shown in Figure 8. It is found that carrier concentration is equal to B

Fig.8.-Relationship between carrier and B concentrations in B-doped $\text{Si}_{1-x}\text{Ge}_x$ films.

Fig.9.-Relationship between resistivity and carrier concentration in B-doped $\text{Si}_{1-x}\text{Ge}_x$ films. Film thicknesses range from 200 to 500nm.

Fig.10.-Relationship between Hall mobility and carrier concentration in B-doped $\text{Si}_{1-x}\text{Ge}_x$ films. Hall mobility in p-Si and p-Ge according to references [13] and [14] are given by the solid lines. Film thicknesses range from 200 to 500nm.

Fig.11.-Relationship among Hall mobility, carrier concentration and $\text{Si}_{0.75}\text{Ge}_{0.25}$ film thickness.

concentration in the range 3×10^{17} – $2 \times 10^{20} \text{ cm}^{-3}$, regardless of the Ge fraction. In the present experiments, electron diffraction measurements showed that B doped $\text{Si}_{1-x}\text{Ge}_x$ 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 $\text{Si}_{0.75}\text{Ge}_{0.25}$ 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 $\text{Si}_{0.75}\text{Ge}_{0.25}$ 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 $\text{Si}_{0.75}\text{Ge}_{0.25}$ 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 $\text{Si}_{0.75}\text{Ge}_{0.25}$ film shown in Figure 11 were independent of current in the range 10^{-6} - 2.5×10^{-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 $\text{Si}_{0.75}\text{Ge}_{0.25}$ film is nearly equal to that of the unstrained one, since it is well known that the critical thickness for $\text{Si}_{0.75}\text{Ge}_{0.25}$ film grown on Si(100) is about 100nm [15].

4.-Conclusions.

B-doped $\text{Si}_{1-x}\text{Ge}_x$ films have been epitaxially grown on Si(100) at 550°C by LPCVD. The incorporation rate of B increases proportionally with increasing B_2H_6 partial pressure and is larger on the deposited $\text{Si}_{1-x}\text{Ge}_x$ 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_2H_6 during $\text{Si}_{1-x}\text{Ge}_x$ 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 3×10^{17} - $2 \times 10^{20} \text{ cm}^{-3}$, regardless of the Ge fraction, and Hall mobility has a minimum value for $\text{Si}_{0.75}\text{Ge}_{0.25}$ film, and the mobility of the strained $\text{Si}_{0.75}\text{Ge}_{0.25}$ film is nearly equal to that of the unstrained one.

Acknowledgments.

The authors wish to express their thanks to Profs. Shoichi Ono and Takashi Matsuura for their advice and encouragement in executing this study. The CVD reactor was provided by Kokusai Electric Co. Ltd. This study was carried out in the Super-clean Room of the Laboratory for Microelectronics, Research Institute of Electrical Communication, Tohoku University, and was partially supported by Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan.

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