

## Low-Temperature Boron-Doped $\text{Si}_{1-x}\text{Ge}_x$ Heteroepitaxy by LPCVD

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$\text{Si}_{1-x}\text{Ge}_x$  heteroepitaxy in a temperature range of 550-700°C is demonstrated by LPCVD using  $\text{Si}_2\text{H}_6/\text{GeH}_4/\text{B}_2\text{H}_6/\text{H}_2$  gas system. B-doping characteristics of  $\text{Si}_{1-x}\text{Ge}_x$ , aimed at applying to npn  $\text{Si}_{1-x}\text{Ge}_x$  base HBTs, are then investigated in detail. The B doping velocity controlled by the  $\text{B}_2\text{H}_6$  partial pressure is independent of the  $\text{Si}_{1-x}\text{Ge}_x$  growth conditions. The resistivity of  $\text{Si}_{1-x}\text{Ge}_x$  doped higher than  $1 \times 10^{20} \text{cm}^{-3}$  is  $1 \times 10^{-3} \Omega \cdot \text{cm}$ . The dislocation density is below  $10^8 \text{cm}^{-2}$ , which is one order lower than that of the undoped  $\text{Si}_{1-x}\text{Ge}_x$ .

### 1. Introduction

$\text{Si}_{1-x}\text{Ge}_x/\text{Si}$  heterostructures are expected to be applied to silicon-based heterostructure devices, Si-HBTs for instance, utilizing their remarkable band-gap differences dependent on the Ge content and the strain.<sup>1-5)</sup>  $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$  heterostructures have been fabricated using chemical vapor deposition (CVD), molecular beam epitaxy (MBE), and solid phase epitaxy (SPE) techniques. The CVD technique is superior to the MBE and the SPE techniques from a productivity and suitability point of view in conventional Si LSI processes. However, the CVD technique using  $\text{SiH}_4$  and  $\text{GeH}_4$  requires temperatures above 900°C.<sup>6,7)</sup> Consequently, such problems arise as strained layer relaxation, interface reaction and impurity diffusion. Reduction in growth temperature has therefore been demanded. So far, rather incoventional CVD techniques such as UHV/CVD and limited reaction processing (LRP) using  $\text{SiH}_4$  and  $\text{SiH}_2\text{Cl}_2$  with  $\text{GeH}_4$ , respectively, have been reported to lower the

growth temperature.<sup>8,9)</sup>

The purpose of the present study is to realize low-temperature heteroepitaxy of  $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$  with a conventional low-pressure CVD (LPCVD) reactor. Heteroepitaxy of B-doped  $\text{Si}_{1-x}\text{Ge}_x$  is investigated especially in detail, since it is essential to fabricating npn  $\text{Si}_{1-x}\text{Ge}_x$  base HBTs. To lower the growth temperature, we adopted two means. One is using  $\text{Si}_2\text{H}_6$  in replacement of  $\text{SiH}_4$  as the source gas of Si. This is because the decomposition probability of  $\text{Si}_2\text{H}_6$  is higher than that of  $\text{SiH}_4$ . The other is hydrogen-flow processing on the Si surface at a growth temperature performed prior to  $\text{Si}_{1-x}\text{Ge}_x$  deposition. This processing promotes the removal of Si oxide on the surface through the reduction reaction with  $\text{Si}_2\text{H}_6$  and  $\text{GeH}_4$ .<sup>10)</sup> In the following, heteroepitaxy achieved in a temperature range of 550-700°C is demonstrated. B-doping characteristics up to  $4 \times 10^{20} \text{cm}^{-3}$  are described.

### 2. Experimental

A horizontal CVD reactor with an infrared lamp heater was used for the experiments. The substrate was a p-type (100) silicon wafer with a resistivity above  $1\text{k } \Omega \cdot \text{cm}$ . The wafer was rinsed with  $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2$ , HF, and  $\text{HCl}/\text{H}_2\text{O}_2$  solutions and set on the susceptor in the reactor just after HF-dip. Purified-hydrogen was supplied on the wafer surface for 5 min at a growth temperature. A  $\text{Si}_{1-X}\text{Ge}_X$  film was grown by introducing  $\text{Si}_2\text{H}_6$  and  $\text{GeH}_4$  with  $\text{H}_2$  carrier gas. For B-doping,  $\text{H}_2$ -based  $\text{B}_2\text{H}_6$  was added to the forming gas. The growth temperature range was  $550\text{--}700^\circ\text{C}$ . In the B-doping experiments, the growth temperature was fixed at  $680^\circ\text{C}$ , because the minimum temperature for Si crystal growth on Ge is  $650^\circ\text{C}$  in the present CVD reactor<sup>11,12</sup>, and it is most convenient in Si-HBT fabrication to perform B-doped  $\text{Si}_{1-X}\text{Ge}_X$  growth and following Si crystal growth at the same temperature. The total pressure during deposition was about 3 Torr.

### 3. Results and Discussion

The epitaxial growth of the  $\text{Si}_{1-X}\text{Ge}_X$  films in a temperature range of  $550\text{--}700^\circ\text{C}$  at constant partial pressures of  $\text{Si}_2\text{H}_6$  ( $5.3 \times 10^{-2}$  Torr) and  $\text{GeH}_4$  ( $1.5 \times 10^{-2}$  Torr) is confirmed by reflection electron diffraction (RED). Germanium content X is almost constant, 0.2, irrespective of growth temperature. Crystallinity of the  $\text{Si}_{1-X}\text{Ge}_X$  films grown at temperatures below  $600^\circ\text{C}$  is better than that above  $630^\circ\text{C}$  as revealed by streaky patterns with Kikuchi lines in the RED photographs. The cross-sectional TEM (XTEM) photographs of the samples formed at  $650^\circ\text{C}$  and  $550^\circ\text{C}$  are shown in Fig. 1. The  $650^\circ\text{C}$ -grown sample includes a great deal of dislocations that originate from the lattice misfit between  $\text{Si}_{0.8}\text{Ge}_{0.2}$  and Si ( $\sim 0.8\%$ ). The dislocation

density is roughly evaluated to be  $4 \times 10^8 \text{cm}^{-2}$ . In contrast with this, the dislocation density of the  $550^\circ\text{C}$ -grown sample decreases to about  $4 \times 10^7 \text{cm}^{-2}$ . This result corresponds to that of the RED patterns.

Fig. 2 shows dependence of the  $\text{Si}_{0.75}\text{Ge}_{0.25}$  growth rate on the growth temperature. The partial pressures of  $\text{Si}_2\text{H}_6$  and  $\text{GeH}_4$  are retained at  $1.5 \times 10^{-2}$  Torr. The activation energy of the growth rate is 1.8eV, which is even larger than an activation energy, 1.4eV, reported<sup>12</sup>) for surface-reaction limited Si growth using a  $\text{Si}_2\text{H}_6/\text{H}_2$  gas system. Therefore, the growth rate of  $\text{Si}_{1-X}\text{Ge}_X$  is considered to be controlled by the  $\text{Si}_2\text{H}_6$  and  $\text{GeH}_4$  surface reaction.

The dependence of the B doping velocity on the  $\text{B}_2\text{H}_6$  partial pressure ( $P_{\text{B}_2\text{H}_6}$ ) under various  $\text{Si}_{1-X}\text{Ge}_X$  growth conditions is shown in Fig. 3. The B doping velocity is defined

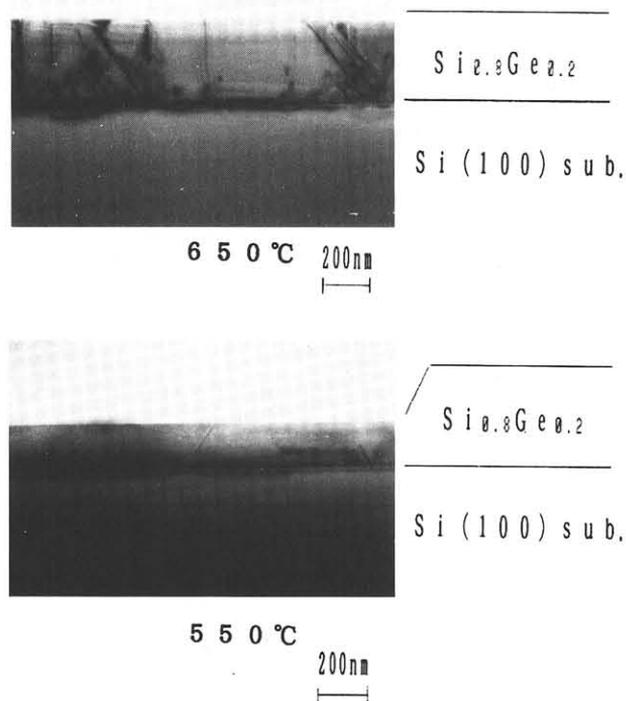


Fig. 1 XTEM Photographs of the  $\text{Si}_{0.8}\text{Ge}_{0.2}$ /Si Heterostructures Formed at  $650^\circ\text{C}$  and  $550^\circ\text{C}$

by the product  $C_B \times R$  of the B concentration ( $C_B$ ) and the  $\text{Si}_{1-x}\text{Ge}_x$  growth rate ( $R$ ). The doping velocity is nearly proportional to  $P_{\text{B}_2\text{H}_6}$ . Besides, no dependence of the doping velocity on the growth condition is observed. These facts suggest that B doping is independent of  $\text{Si}_{1-x}\text{Ge}_x$  growth and the B doping velocity is controlled by  $\text{B}_2\text{H}_6$  supply onto the surface.

Fig. 4 shows the dependence of the  $\text{Si}_{1-x}\text{Ge}_x$  resistivity on  $C_B$ . The  $C_B$  is determined by the  $\text{B}_2\text{H}_6$  partial pressure. Boron atoms can be doped into  $\text{Si}_{1-x}\text{Ge}_x$  up to  $C_B = 4 \times 10^{20} \text{ cm}^{-3}$ . The minimum resistivity of  $1 \times 10^{-3} \Omega \cdot \text{cm}$  is obtained with epitaxial  $\text{Si}_{1-x}\text{Ge}_x$  films doped with B above  $1 \times 10^{20} \text{ cm}^{-3}$ . The polycrystalline  $\text{Si}_{1-x}\text{Ge}_x$  films (dashed line) show a high resistivity, compared with that of crystalline films (solid line). Little resistivity change is observed for these samples after the heat-treatment at  $800^\circ \text{C}$  for 10 min in  $\text{N}_2$ .

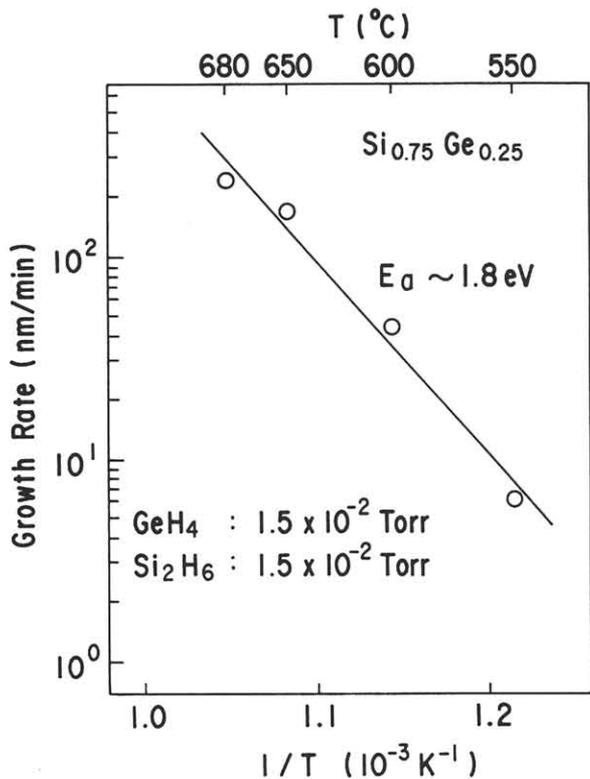


Fig. 2 Growth Temperature Dependence of the  $\text{Si}_{0.75}\text{Ge}_{0.25}$  Growth Rate

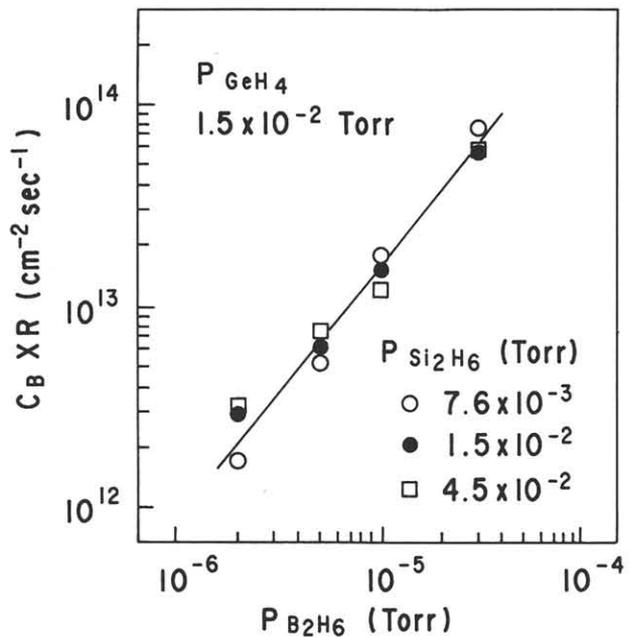


Fig. 3  $P_{\text{B}_2\text{H}_6}$  Dependence of B Doping Velocity

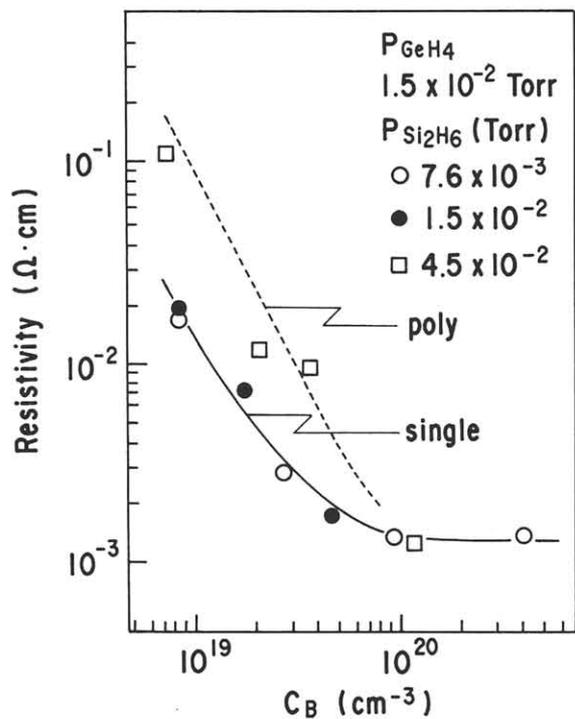


Fig. 4 B Concentration Dependence of Resistivity

Fig. 5 shows the XTEM photographs of undoped and highly B-doped ( $\sim 1 \times 10^{20} \text{cm}^{-3}$ )  $\text{Si}_{0.75}\text{Ge}_{0.25}$  films on Si(100) substrates. The film thicknesses are 180 nm and 150 nm. They are larger than the critical thickness reported in the literature<sup>13,14</sup>). A great deal of dislocations, originating from the lattice misfit ( $\sim 1\%$ ), are observed in the undoped film, which is similar to the upper (650°C-grown) photograph in Fig. 1. It is seen, on the other hand, that the dislocations drastically decrease by high B doping. The dislocation density is roughly evaluated below  $10^8 \text{cm}^{-2}$ . The reason for the crystallinity improvement is considered to be that the doped B atoms reduce the strain of  $\text{Si}_{1-x}\text{Ge}_x$  layer on Si. Detail investigation is necessary to verify this.

#### 4. Conclusion

The heteroepitaxy is demonstrated in a

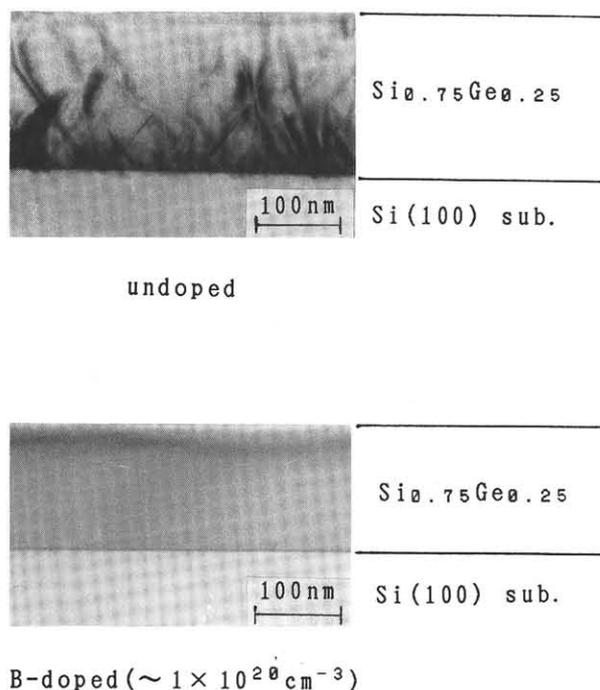


Fig. 5 XTEM Photographs of the Undoped and Highly B-doped ( $1 \times 10^{20} \text{cm}^{-3}$ )  $\text{Si}_{0.75}\text{Ge}_{0.25}$ /Si Heterostructures Formed at 680°C

temperature range of 550-700°C. The dislocation density of undoped 550°C-grown  $\text{Si}_{0.8}\text{Ge}_{0.2}$  is  $\sim 4 \times 10^7 \text{cm}^{-2}$ . The growth rate is controlled by the  $\text{Si}_2\text{H}_6$  and  $\text{GeH}_4$  surface reaction. Its activation energy is  $\sim 1.8 \text{eV}$ . B-doping characteristics are investigated at a growth temperature of 680°C. The B doping is independent of the  $\text{Si}_{1-x}\text{Ge}_x$  growth. The minimum resistivity of  $1 \times 10^{-3} \Omega \cdot \text{cm}$  is obtained in highly B-doped  $\text{Si}_{1-x}\text{Ge}_x$  ( $> 1 \times 10^{20} \text{cm}^{-3}$ ). The dislocation density of highly B-doped films decreases below  $10^8 \text{cm}^{-2}$ , although a great deal of dislocations, originating from the lattice misfit ( $\sim 1\%$ ), are observed in the undoped films grown at 680°C.

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