

# Donor-doping characteristics of gas-source molecular beam epitaxial Si and Si<sub>1-x</sub>Ge<sub>x</sub> using phosphine

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Well-behaved and reproducible *n*-type doping of Si and Si<sub>1-x</sub>Ge<sub>x</sub> by phosphine during gas-source molecular beam epitaxy is demonstrated. No significant reduction of growth rate of these materials in the presence of phosphine is recorded in the doping range of 10<sup>17</sup>–10<sup>19</sup> cm<sup>-3</sup> and perfect surface morphologies are observed. The incorporated P atoms are fully activated without *ex situ* annealing. The doping profiles are well defined in both Si and Si<sub>1-x</sub>Ge<sub>x</sub> layers. A *p*-Si<sub>0.9</sub>Ge<sub>0.1</sub>/*n*-Si heterojunction diode made with boron and phosphine doping has demonstrated excellent rectifying characteristics.

## I. INTRODUCTION

Epitaxial growth of Si and Si<sub>1-x</sub>Ge<sub>x</sub> layers on Si substrates by various techniques<sup>1-7</sup> has recently been studied extensively. While control of the layer composition and thickness has been reported to be successful in each technique, the control of doping, and especially *n*-type doping, still remains somewhat elusive. In solid-source molecular beam epitaxy (MBE), for example, the most commonly used dopant is antimony (Sb). However, Sb doping suffers from a small and temperature-dependent sticking coefficient and strong surface segregation.<sup>8,9</sup> Elemental arsenic (As) and phosphorus (P) are not suitable in conventional MBE because their vapor pressures are too high. In chemical vapor deposition (CVD), phosphine (PH<sub>3</sub>) and arsine (AsH<sub>3</sub>) are the commonly used dopants. However, despite the fact that *n*-type doping densities as high as 10<sup>20</sup> cm<sup>-3</sup> can be easily achieved, the use of hydrides tends to change the chemistry of the growing Si and Si<sub>1-x</sub>Ge<sub>x</sub> surfaces, thereby suppressing the decomposition of silane (SiH<sub>4</sub>) or disilane (Si<sub>2</sub>H<sub>6</sub>). This leads to reduced growth rates, unstable incorporation efficiency, and/or poor surface morphology.<sup>10</sup> Although it is known that the surface chemistry can be changed at different growth pressures, till date the surface poisoning problems have not been eliminated for growth in the pressure range of 10<sup>-3</sup> Torr (high vacuum) to 760 Torr (1 atm).<sup>11-13</sup>

Gas-source MBE is an attractive alternative for the epitaxy of Si and Si<sub>1-x</sub>Ge<sub>x</sub> layers. In this technique growth is done at the pressures of 10<sup>-5</sup>–10<sup>-7</sup> Torr, which are two orders of magnitude lower than those for ultrahigh vacuum CVD. Hirayama and Tatsumi<sup>14</sup> have demonstrated that *n*-type doping of Si using PH<sub>3</sub> is feasible. These authors used 5% PH<sub>3</sub> diluted in SiH<sub>4</sub> as the dopant source. The pressure during their growth was less than 2×10<sup>-5</sup> Torr. It was observed that the Si growth rate is reduced in the presence of PH<sub>3</sub>. However, the doping levels used were greater than 1×10<sup>19</sup> cm<sup>-3</sup> and they did not study the doping of Si<sub>1-x</sub>Ge<sub>x</sub>. In this work, we report the results on *n*-type doping of both Si and Si<sub>1-x</sub>Ge<sub>x</sub> in the doping range of 10<sup>17</sup>–10<sup>19</sup> cm<sup>-3</sup>. We have used PH<sub>3</sub> (100 ppm) diluted in H<sub>2</sub> as the dopant source, and Si<sub>2</sub>H<sub>6</sub> and elemental Ge as the Si and Ge sources, respectively. It is found that there is no significant reduction in growth rate in the presence of PH<sub>3</sub> for either Si or Si<sub>1-x</sub>Ge<sub>x</sub>.

## II. EXPERIMENTAL TECHNIQUES

A multiple-chamber RIBER 32 MBE with vacuum load locks has been used in our experiments. The growth chamber is provided with an ion pump which maintains a background vacuum of 10<sup>-10</sup> Torr. The cryoshroud temperature is fixed at 77 K and additional pumping is provided during growth by a turbomolecular pump. The Si<sub>2</sub>H<sub>6</sub> and PH<sub>3</sub>/H<sub>2</sub> flow rates are controlled by precision mass flow controllers. The gases are not precracked. The elemental Ge is effused from a resistively heated cell with a PBN crucible.<sup>2</sup> The substrate temperature is monitored during growth by a pyrometer.

Si and Si<sub>1-x</sub>Ge<sub>x</sub> epitaxial layers were grown on (100)-oriented, B-doped (*p*-type) or P-doped (*n*-type) Si wafers having resistivity between 50 and 100 Ω cm. Before growth, the surface oxide was removed by heating to 840 °C for 10 min. At this point a clear (2×1) reflection high electron energy diffraction (RHEED) pattern is observed. During growth, the chamber pressure is between 5×10<sup>-6</sup> and 4×10<sup>-5</sup> Torr, depending on the Si<sub>2</sub>H<sub>6</sub> and PH<sub>3</sub> flow rates. The growth temperature is fixed at 700 °C. After growth, the compositions of the epitaxial layers are confirmed by double-crystal x-ray diffraction (XRD). The doping density of the uniformly doped samples was determined by Hall measurements.<sup>15</sup> Doping profiles were measured by both spreading resistance analysis (SRA, by Solecon Laboratories, San Jose, California) and secondary-ion-mass spectrometry (SIMS, by Evans East, Plainsboro, New Jersey). For the latter, the P concentration profiles are determined chemically. For the former, the variation of carrier concentration (or resistivity) versus depth is obtained electrically.

## III. RESULTS AND DISCUSSION

The variation of the electron concentration is plotted against the PH<sub>3</sub> flow rate in Fig. 1 for uniformly doped Si samples. The P-doped layers are all *n*-type without *ex situ* annealing. It is evident that the electron concentration is proportional to the PH<sub>3</sub> flow rate. The surface morphology is mirror-like for the entire doping range. The doping profiles in a uniformly PH<sub>3</sub>-doped Si layer on a *p*-type Si substrate, obtained from both SIMS and SRA, are presented in Fig. 2. It is seen that the profiles measured by the two techniques are

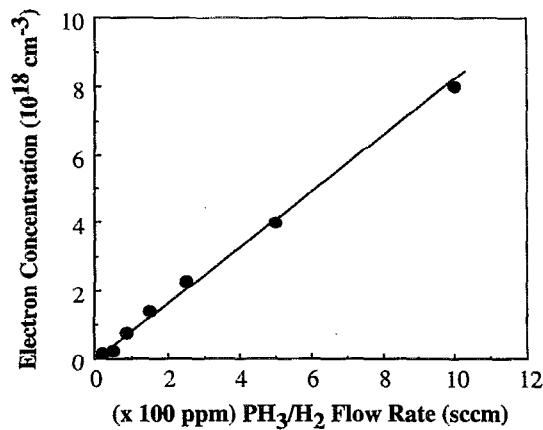


FIG. 1. Dependence of Hall electron concentration on  $\text{PH}_3$  flow rate in gas-source MBE of Si using  $\text{Si}_2\text{H}_6$  (7 sccm).

in good agreement. The incorporated P atoms are therefore  $\sim 100\%$  electrically activated. Only the SRA results are presented below for simplicity.

The doping and resistivity profiles in a Si sample are shown in Fig. 3. The entire layer is grown in incremental steps of increasing  $\text{Si}_2\text{H}_6$  flow rates, while the  $\text{PH}_3$  flow rate is kept fixed at 2 sccm. The  $\text{Si}_2\text{H}_6$  flow rate was successively fixed at 7, 14, 30, and 55 sccm. For each  $\text{Si}_2\text{H}_6$  flow rate, the  $\text{PH}_3$  flow was switched on and off. The growth time  $t$  was proportionally reduced as the  $\text{Si}_2\text{H}_6$  flow rate was increased. It was found that the growth rate (the thickness of each layer divided by  $t$ ) is a function of the  $\text{Si}_2\text{H}_6$  flow rate. However, unlike reports made earlier by most groups using the CVD technique<sup>10-13</sup> that the growth rate is reduced in the presence of  $\text{PH}_3$ , we find that the growth rate is not significantly affected. The doping profile is well defined except in the incremental layers grown with a  $\text{Si}_2\text{H}_6$  flow rate of 55 sccm when the growth rate is too high ( $\sim 1000 \text{ \AA}/\text{min}$ ). The doping concentration is not affected by the  $\text{Si}_2\text{H}_6$  flow rate, but is determined almost exclusively by the  $\text{PH}_3$  flow rate. It is also observed that the  $n$ -doping level goes down only to a level of  $2 \times 10^{17} \text{ cm}^{-3}$  when  $\text{PH}_3$  is shut off, indicating that there is a high level of residual  $\text{PH}_3$  in the system, which gets incor-

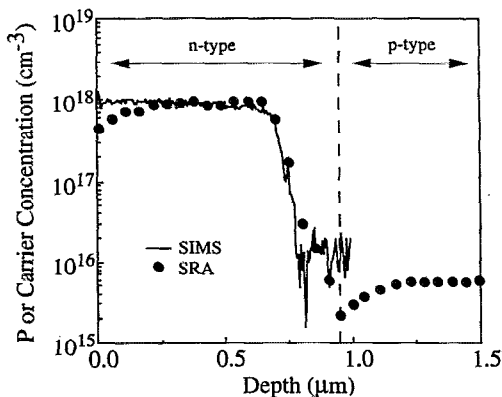


FIG. 2.  $n$ -type doping profiles measured by SIMS and SRA in a uniformly doped sample.

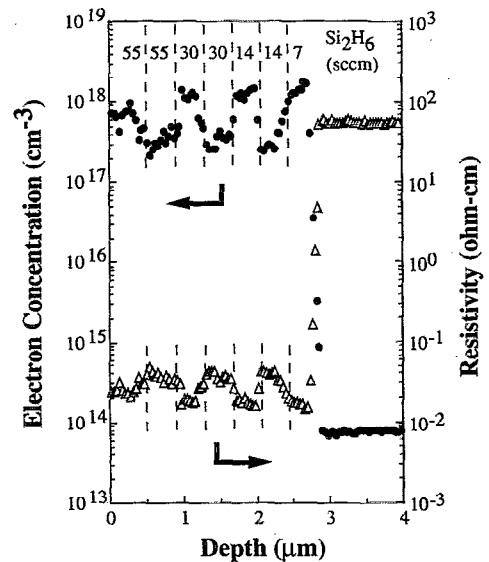


FIG. 3. Spreading resistance analysis data of the  $n$ -doping profile in a  $\text{PH}_3$ -doped Si sample. The growth sequence was 3500  $\text{Å}$   $n$ -doped Si, 3500  $\text{Å}$  undoped Si, 3500  $\text{Å}$   $n$ -doped Si, 3500  $\text{Å}$  undoped Si, 3500  $\text{Å}$   $n$ -doped Si, 3500  $\text{Å}$  undoped Si, and 3500  $\text{Å}$   $n$ -doped Si.

porated in the growing layer. While this high level of  $n$  doping in the data may partly be due to a lack of resolution in the measurement, the effect primarily originates from inadequate pumping of  $\text{PH}_3$ . Therefore, in heterostructures where abrupt isotype and anisotype doping profiles are required, such as in bipolar transistors and junction diodes, growth interruption may be necessary.

Figure 4 shows similar data obtained in a  $\text{Si}_{0.9}\text{Ge}_{0.1}$  sample. Here, the  $\text{Si}_2\text{H}_6$  flow rate was fixed at 14 sccm, and the Ge cell temperature was fixed at 1060  $^\circ\text{C}$ . The  $\text{PH}_3$  flow

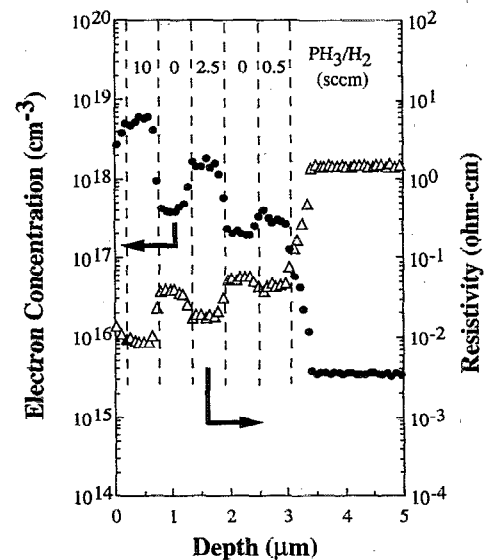


FIG. 4. Spreading resistance analysis data of the  $n$ -doping profile in a  $\text{PH}_3$ -doped  $\text{Si}_{0.9}\text{Ge}_{0.1}$  sample. The growth sequence was Si buffer layer, 6000  $\text{Å}$   $n$ -doped  $\text{Si}_{0.9}\text{Ge}_{0.1}$ , 6000  $\text{Å}$  undoped  $\text{Si}_{0.9}\text{Ge}_{0.1}$ , 6000  $\text{Å}$   $n$ -doped  $\text{Si}_{0.9}\text{Ge}_{0.1}$ , 6000  $\text{Å}$  undoped  $\text{Si}_{0.9}\text{Ge}_{0.1}$ , 6000  $\text{Å}$   $n$ -doped  $\text{Si}_{0.9}\text{Ge}_{0.1}$ , and 1000  $\text{Å}$  undoped  $\text{Si}_{0.9}\text{Ge}_{0.1}$ .

0.2 $\mu\text{m}$ PH <sub>3</sub> -doped Si (n-type, $2 \times 10^{18} \text{ cm}^{-3}$ )
2 $\mu\text{m}$ PH <sub>3</sub> -doped Si (n-type, $1 \times 10^{17} \text{ cm}^{-3}$ )
0.1 $\mu\text{m}$ B-doped Si <sub>0.9</sub> Ge <sub>0.1</sub> (p-type, $1 \times 10^{19} \text{ cm}^{-3}$ )
B-doped Si Substrate (p-type, $1 \times 10^{15} \text{ cm}^{-3}$ )

(a)

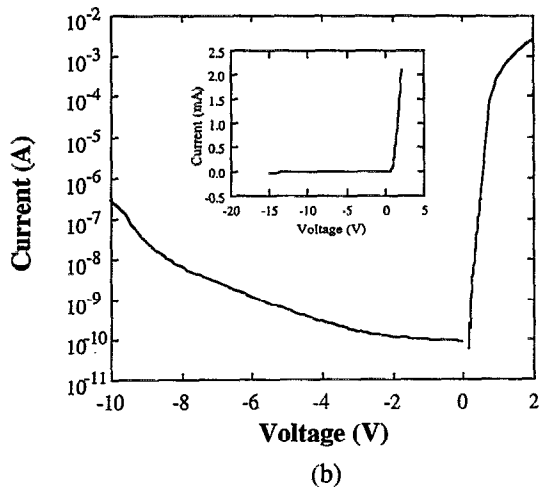


FIG. 5. (a) Schematic of heterostructure  $p$ - $n$  junction diode grown with boron/phosphine doping, and (b) its current-voltage characteristics. The inset in Fig. (b) shows the oscilloscope trace of the rectifying characteristics.

rate was successively changed to 0.5, 2.5, and 10 sccm. For each PH<sub>3</sub> flow rate, the gas flow is switched on and off. Again, it is found that the growth rates with and without PH<sub>3</sub> are similar. The doping concentration increases with increasing PH<sub>3</sub> flow rates, as expected from the data of Fig. 1. Similar doping studies have also been done for other Si<sub>1-x</sub>Ge<sub>x</sub> layers ( $0 \leq x \leq 0.2$ ). The results are the same, i.e., the growth rate is not affected by PH<sub>3</sub> doping.

We have also studied the current-voltage characteristics of a Si<sub>0.9</sub>Ge<sub>0.1</sub>/Si  $p$ - $n$  junction diode grown by using phosphine as the  $n$ -type dopant. The diode structure is shown in Fig. 5(a). The  $p$ -type dopant used was solid B, which has been described previously.<sup>15</sup> The mesa-shaped diodes were fabricated by standard reactive ion etching and Al/Ti/Au metallization was used for the ohmic contacts. The typical  $I$ - $V$  characteristics are shown in Fig. 5(b). The measured turn-on voltage is 0.8 V and the ideality factor is  $\sim 1.7$ . The reverse leakage current at  $-10$  V is less than  $1 \mu\text{A}$ . The large

value of the ideality factor may result from many causes. We believe that the most dominant one is the large series resistance from the ohmic contacts.

To explain the apparent discrepancy between our result and that of Hirayama and Tatsumi,<sup>14</sup> who observed a decrease in growth rate in the presence of PH<sub>3</sub>, one has to consider the nature of the PH<sub>3</sub> sources. By comparison, our source of P atoms is more diluted than that of Hirayama and Tatsumi. Thus, the optimal amount of PH<sub>3</sub> is cracked on the surface, to produce P atoms which are incorporated on lattice sites with a unity sticking coefficient. Excess PH<sub>3</sub> and P atoms on the surface may prevent the dissociation of SiH<sub>4</sub> or Si<sub>2</sub>H<sub>6</sub>, resulting in a reduced growth rate.

#### IV. CONCLUSION

We have demonstrated the  $n$  doping using PH<sub>3</sub> in gas-source MBE of Si and Si<sub>1-x</sub>Ge<sub>x</sub>. Doping levels between  $10^{17}$  and  $10^{19} \text{ cm}^{-3}$  have been reproducibly obtained. The incorporated P atoms are completely activated, based on both SIMS and SRA data. It is observed that the Si and Si<sub>1-x</sub>Ge<sub>x</sub> growth rates are not significantly affected by the presence of PH<sub>3</sub>, which is believed to be due to extremely low PH<sub>3</sub> partial pressures during growth. Excellent rectifying characteristics have been observed in Si<sub>0.9</sub>Ge<sub>0.1</sub>/Si  $p$ - $n$  junction diodes.

#### ACKNOWLEDGMENTS

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- J. C. Bean, *J. Cryst. Growth* **81**, 411 (1987).
- S. H. Li, P. K. Bhattacharya, R. Malik, and E. Gulari, *J. Electron. Mater.* **22**, 793 (1993).
- H. Hirayama, M. Hiroi, K. Koyama, and T. Tatsumi, *Appl. Phys. Lett.* **56**, 1107 (1990).
- B. S. Meyerson, *Appl. Phys. Lett.* **48**, 797 (1986).
- J. H. Comfort, L. M. Garverick, and R. Reif, *J. Appl. Phys.* **62**, 3388 (1987).
- J. C. Sturm, P. V. Schwartz, E. J. Prinz, and H. Manoharan, *J. Vac. Sci. Technol. B* **9**, 2011 (1991).
- D. A. Gruntzmacher, T. O. Sedgwick, A. Zaslavsky, A. R. Powell, R. A. Kiehl, W. Ziegler, and J. Cotte, *J. Electron. Mater.* **22**, 303 (1993).
- R. A. Metzger and F. G. Allen, *J. Appl. Phys.* **55**, 931 (1984).
- J. C. Bean, *Appl. Phys. Lett.* **33**, 654 (1978).
- B. S. Meyerson and M. L. Yu, *J. Electrochem. Soc.* **131**, 2366 (1984).
- M. Racanelli and D. W. Greve, *J. Vac. Sci. Technol. B* **9**, 2017 (1991).
- S. M. Jang, K. Liao, and R. Reif, *Appl. Phys. Lett.* **63**, 1675 (1993).
- D. W. Greve, *Mater. Sci. Eng. B* **18**, 22 (1993).
- H. Hirayama and T. Tatsumi, *Appl. Phys. Lett.* **55**, 131 (1989).
- S. H. Li, P. K. Bhattacharya, S. W. Chung, J. X. Jou, and E. Gulari, *J. Electron. Mater.* **22**, 409 (1993).