Donor-doping characteristics of gas-source molecular beam epitaxial Si and Si$_{1-x}$Ge$_x$ using phosphine

S. H. Li and P. K. Bhattacharya
Solid-State Electronics Laboratory, Department of Electrical Engineering and Computer Science, University of Michigan, Ann Arbor, Michigan 48109-2122

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Well-behaved and reproducible n-type doping of Si and Si$_{1-x}$Ge$_x$ 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 $10^{17}$ to $10^{19}$ cm$^{-3}$ 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$_{1-x}$Ge$_x$ layers. A p-Si$_{0.9}$Ge$_{0.1}$/n-Si heterojunction diode made with boron and phosphine doping has demonstrated excellent rectifying characteristics.

I. INTRODUCTION

Epitaxial growth of Si and Si$_{1-x}$Ge$_x$ layers on Si substrates by various techniques 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 serious surface segregation. 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$_3$) and arsine (AsH$_3$) are the commonly used dopants. However, despite the fact that n-type doping densities as high as $10^{20}$ cm$^{-3}$ can be easily achieved, the use of hydrides tends to change the chemistry of the growing Si and Si$_{1-x}$Ge$_x$ surfaces, thereby suppressing the decomposition of silane (SiH$_4$) or disilane (Si$_2$H$_6$). This leads to reduced growth rates, unstable incorporation efficiency, and/or poor surface morphology. 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 $10^{-3}$ Torr (high vacuum) to 760 Torr (1 atm).

Gas-source MBE is an attractive alternative for the epitaxy of Si and Si$_{1-x}$Ge$_x$ layers. In this technique growth is done at the pressures of $10^{-5}$ to $10^{-7}$ Torr, which are two orders of magnitude lower than those for ultra-high vacuum CVD. Hirayama and Tatsumi have demonstrated that n-type doping of Si using PH$_3$ is feasible. These authors used 5% PH$_3$ diluted in SiH$_4$ as the dopant source. The pressure during their growth was less than $2 \times 10^{-5}$ Torr. It was observed that the Si growth rate is reduced in the presence of PH$_3$. However, the doping levels used were greater than $1 \times 10^{19}$ cm$^{-3}$ and they did not study the doping of Si$_{1-x}$Ge$_x$. In this work, we report the results on n-type doping of both Si and Si$_{1-x}$Ge$_x$ in the doping range of $10^{17}$ to $10^{19}$ cm$^{-3}$. We have used PH$_3$ (100 ppm) diluted in H$_2$ as the dopant source, and SiH$_4$ 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$_3$ for either Si or Si$_{1-x}$Ge$_x$.

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 $10^{-10}$ Torr. The cryoshroud temperature is fixed at 77 K and additional pumping is provided during growth by a turbomolecular pump. The SiH$_4$ and PH$_3$/H$_2$ 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. The substrate temperature is monitored during growth by a pyrometer.

Si and Si$_{1-x}$Ge$_x$ epitaxial layers were grown on (100)-oriented, B-doped (p-type) or P-doped (n-type) Si wafers having resistivity between 50 and 100 $\Omega$ 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 $5 \times 10^{-6}$ and $4 \times 10^{-3}$ Torr, depending on the SiH$_4$ and PH$_3$ 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. 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$_3$ 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$_3$ flow rate. The surface morphology is mirror-like for the entire doping range. The doping profiles in a uniformly PH$_3$-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 PH$_3$/H$_2$ flow rate in gas-source MBE of Si using Si$_2$H$_6$ (7 sccm). in good agreement. The incorporated P atoms are therefore ~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 Si$_2$H$_6$ flow rates, while the PH$_3$ flow rate is kept fixed at 2 sccm. The Si$_2$H$_6$ flow rate was successively fixed at 7, 14, 30, and 55 sccm. For each Si$_2$H$_6$ flow rate, the PH$_3$ flow was switched on and off. The growth time $t$ was proportionally reduced as the Si$_2$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 Si$_2$H$_6$ flow rate. However, unlike reports made earlier by most groups using the CVD technique$^{10-13}$ that the growth rate is reduced in the presence of 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 Si$_2$H$_6$ flow rate of 55 sccm when the growth rate is too high ( ~1000 Å/min). The doping concentration is not affected by the Si$_2$H$_6$ flow rate, but is determined almost exclusively by the PH$_3$ flow rate. It is also observed that the $n$-doping level goes down only to a level of $2\times10^{17}$ cm$^{-3}$ when PH$_3$ is shut off, indicating that there is a high level of residual PH$_3$ in the system, which gets incor-

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

FIG. 4. Spreading resistance analysis data of the $n$-doping profile in a PH$_3$-doped Si$_{0.9}$Ge$_{0.1}$ sample. The growth sequence was Si buffer layer, 6000 Å $n$-doped Si$_{0.9}$Ge$_{0.1}$, 6000 Å undoped Si$_{0.9}$Ge$_{0.1}$, 6000 Å $n$-doped Si$_{0.9}$Ge$_{0.1}$, 6000 Å undoped Si$_{0.9}$Ge$_{0.1}$, 6000 Å $n$-doped Si$_{0.9}$Ge$_{0.1}$, and 1000 Å undoped Si$_{0.9}$Ge$_{0.1}$.
rate was successively changed to 0.5, 2.5, and 10 sccm. For each PH₃ flow rate, the gas flow is switched on and off. Again, it is found that the growth rates with and without PH₃ are similar. The doping concentration increases with increasing PH₃ flow rates, as expected from the data of Fig. 1. Similar doping studies have also been done for other Si₀.₅Ge₀.₅ layers (0 ≤ x ≤ 0.2). The results are the same, i.e., the growth rate is not affected by PH₃ doping.

We have also studied the current-voltage characteristics of a Si₀.₅Ge₀.₅/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. 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 ~1.7. The reverse leakage current at ~10 V is less than 1 μA. 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, who observed a decrease in growth rate in the presence of PH₃, one has to consider the nature of the PH₃ sources. By comparison, our source of P atoms is more diluted than that of Hirayama and Tatsumi. Thus, the optimal amount of PH₃ is cracked on the surface, to produce P atoms which are incorporated on lattice sites with a unity sticking coefficient. Excess PH₃ and P atoms on the surface may prevent the dissociation of SiH₄ or Si₂H₆, resulting in a reduced growth rate.

IV. CONCLUSION

We have demonstrated the n doping using PH₃ in gas-source MBE of Si and Si₀.₅Ge₀.₅. Doping levels between 10¹⁷ and 10¹⁹ 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 Si₀.₅Ge₀.₅ growth rates are not significantly affected by the presence of PH₃, which is believed to be due to extremely low PH₃ partial pressures during growth. Excellent rectifying characteristics have been observed in Si₀.₅Ge₀.₅/Si p-n junction diodes.

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