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Chemical beam epitaxial growth of Si-doped GaAs and InP by using silicon tetraiodide

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Silicon tetraiodide (SiI_4), which has a very weak Si-I bond strength (70 kcal/mol), is successfully employed as a novel Si dopant in the chemical beam epitaxy of GaAs and InP. No precracking is necessary before supplying SiI_4 with He carrier gas. High electrical quality is ascertained for both GaAs and InP with linear Si doping controllability in the range from 2×10^{16} to $6 \times 10^{18} \text{ cm}^{-3}$ with a uniformity of less than 2% within a 3-in.-diam area. The electron mobility in a GaAs with a carrier concentration of $1 \times 10^{17} \text{ cm}^{-3}$ is $4400 \text{ cm}^2/\text{V s}$ and that in InP with a carrier concentration of $4 \times 10^{17} \text{ cm}^{-3}$ is $2400 \text{ cm}^2/\text{V s}$, respectively. Abrupt interfaces and precise on-off controllability without any memory effect is also confirmed by secondary-ion-mass, spectroscopy measurements. The electrical activation ratio of Si in SiI_4 for both GaAs and InP is almost 100% in the range studied here. These versatile features suggest that SiI_4 is a promising candidate as a Si dopant source for chemical beam epitaxy growth. © 1996 American Institute of Physics.
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Silicon (Si) is one of the most commonly used *n*-type dopants for III-V compound semiconductors due to its low thermal diffusivity and low surface segregation. Elemental Si in a Knudsen cell is often used for Si doping in conventional molecular beam epitaxy (MBE) and gas source MBE (GS-MBE), while it cannot be used in chemical beam epitaxy (CBE) or metalorganic molecular beam epitaxy (MOMBE) due to the organic passivation of the Si atoms.¹ The preferred vapor source of Si used mainly for metalorganic chemical vapor deposition (MOCVD) is SiH_4 and Si_2H_6 . The precracking of SiH_4 is required for efficient doping in InP and InGaAs for use in CBE because growth temperature is approximately 100 °C lower than that for GaAs.² Since Si_2H_6 is found to be easily decomposed compared to SiH_4 , Si_2H_6 has been mainly used for the growth of InP-related materials.³⁻⁵ The carrier concentration up to $1.4 \times 10^{18} \text{ cm}^{-3}$ was obtained with CBE-grown InP by Si_2H_6 .⁵ Controllability especially at a low-doping level, however, is still insufficient for device applications as the collector layer of heterojunction bipolar transistor (HBT). Many researchers have experimented with various dopant sources, such as triethylsilane (TESiH),⁶ diethyltelluride (DETe),⁶ tetraethyltin (TESn),^{6,7} and tertiarybutyloctasilacubane [(tBuSi)₈].⁸ Recently, it has been reported that Si doping efficiency and controllability are improved for InP and InGaAs growth by using silicon tetrabromide (SiBr_4),^{9,10} which has a relatively weak (87.9 kcal/mol) Si-Br bond strength,¹¹ which suggests that the facile decomposition of Si is inevitable for a Si dopant source.

In this letter, we show the versatility of silicon tetraiodide (SiI_4), which has a very weak Si-I bond strength (70 kcal/mol)¹¹ as a novel Si dopant source for CBE growth of GaAs and InP through the electrical characterization.

Si-doped GaAs and InP were grown by CBE on undoped GaAs and Fe-doped InP(100) 3-in.-diam substrates. The GaAs layer was grown at 510 °C with a growth rate of 0.65

$\mu\text{m/h}$ by using triethylgallium (TEGa) and arsine (AsH_3). The InP layer was grown at 460 °C with a growth rate of 0.5 $\mu\text{m/h}$ by using trimethylindium (TMIn) and phosphine (PH_3). The Si dopant was specially provided 5N grade purity SiI_4 , which was supplied with helium (He) carrier gas through a mass flow controller without any precracking. The boiling and melting points of SiI_4 are 288 and 120.5 °C, respectively. Here 10% Si_2H_6 diluted with hydrogen (H_2) was used as a reference in some experiments. Hall measurements have been performed at room temperature using the Van der Pauw method to determine the net electron concentration and mobility. Secondary-ion-mass spectrometry (SIMS) was performed with Cs^+ beam to evaluate the Si doping profile.

Figure 1 shows the dependence of the net carrier concentration and electron mobility in GaAs and InP on flow rate of SiI_4 diluted with He carrier gas. The net electron concentration increases from 2.0×10^{16} (at 0.2 sccm) to $2.7 \times 10^{18} \text{ cm}^{-3}$ (at 10 sccm) in GaAs and from 3.7×10^{17} (at 1 sccm) to $5.7 \times 10^{18} \text{ cm}^{-3}$ (at 10 sccm) in InP (at the SiI_4

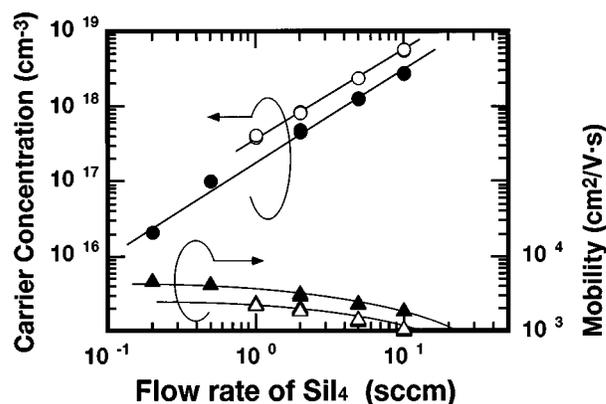


FIG. 1. Dependence of net carrier concentration and electron mobility in GaAs (○, △) and InP (●, ▲) on flow rate of SiI_4 diluted with He carrier gas. The temperature of SiI_4 bubbler was maintained at 50 °C.

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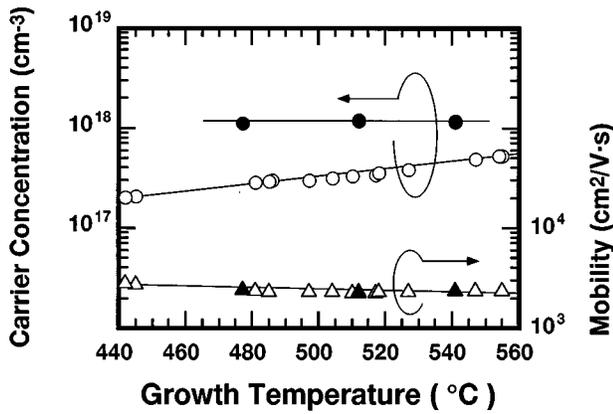


FIG. 2. Net carrier concentration and electron mobility of *n*-GaAs doped by Si₄ (●, ▲) and Si₂H₆ (○, △) as a function of growth temperature. The AsH₃ flow rate was maintained at 4.5 sccm.

temperature of 50 °C). High electrical quality was obtained for both GaAs and InP with linear Si doping controllability. The different Si incorporation efficiency between GaAs and InP at the same Si₄ flow rate was due to the machine's configuration. The higher the temperature Si₄ goes, the higher the net carrier concentration becomes with the activation energy of 1.6 eV (at 2 sccm). The maximum net carrier concentrations obtained for GaAs and InP were 6.1×10^{18} at 7 sccm and $1.7 \times 10^{19} \text{ cm}^{-3}$ with a Si₄ flow rate of 10 sccm at 60 °C. Since the flow rate of Si₄ in our CBE system is controllable in the range between 0.2 and 10 sccm, precise doping control can be achieved in the range between 2×10^{16} and $2.7 \times 10^{18} \text{ cm}^{-3}$ in GaAs, which are adequate for the collector and emitter of AlGaAs/GaAs or InGaP/GaAs heterojunction bipolar transistor (HBT), respectively. Surface morphology is quite fine as well, even for heavily Si-doped GaAs and InP. The electron mobilities of the GaAs layers doped by Si₄ are comparable to these using elemental Si. These InP layers are also comparable to these reported by such as Jackson *et al.*⁹ The dependence of the net carrier concentration and mobility for *n*-GaAs layers grown by using Si₄ on the growth temperature and III/V ratio is com-

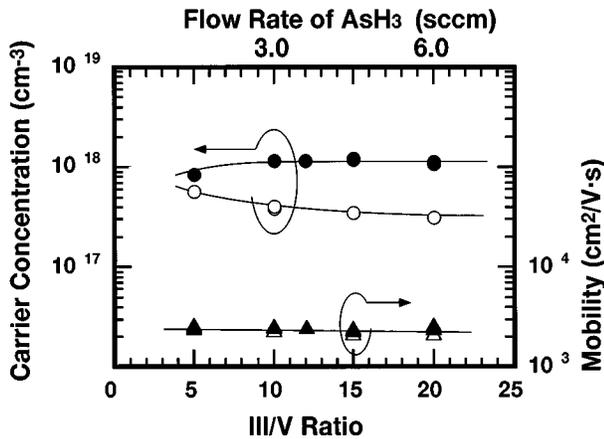


FIG. 3. Net carrier concentration and electron mobility of *n*-GaAs doped by Si₄ (●, ▲) and Si₂H₆ (○, △) as a function of III/V ratio. The growth temperature was maintained at 510 and 520 °C for using Si₄ and Si₂H₆, respectively.

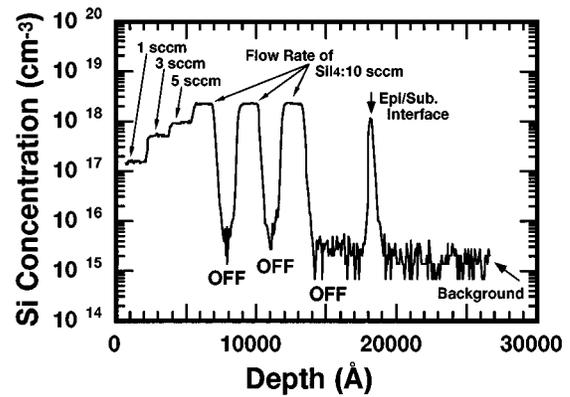


FIG. 4. SIMS profile of Si-modulation-doped GaAs layer by using Si₄.

pared in Figs. 2 and 3 with those for *n*-GaAs layers grown by using Si₂H₆. The net carrier concentration of GaAs layers grown by Si₄ is constant in the entire growth temperature and III/V ratio ranges investigated, in contrast to Si₂H₆ doping. This results in excellent uniformity. The uniformity of the sheet resistance, defined by (standard deviation/average) over 3-in.-diam *n*-GaAs and *n*-InP layers grown by Si₄, is less than 2%, while that by Si₂H₆ is higher than 8%.

Figure 4 shows the SIMS profile of a Si-modulation-doped GaAs layer by using Si₄. Abrupt interfaces and precise on-off controllability were obtained without any memory effect. In addition the Si concentration was held constant in each doped region step. Furthermore, Si₄ does not introduce any other impurities, such as iodine, oxygen, or sulfur. The relation between carrier concentration and Si concentration in Si-doped GaAs by using Si₄ and Si₂H₆, and Si-doped InP by using Si₄ is shown in Fig. 5. The electrical activation ratio of Si in Si₄ for both GaAs and InP is almost 100% in the range studied, while that in Si₂H₆ is 80% or less. These versatile features are thought to be due to the very weak Si-I bond strength in Si₄ (70 kcal/mol). On the other hand, Si in Si₂H₆ has a Si-Si bond and three Si-H bonds whose energy is stronger than the Si-I bond, which might promote atomic Si formation and incorporation into GaAs and InP.

The growth rates for both GaAs and InP were constant over a wide doping range, indicating that there was little

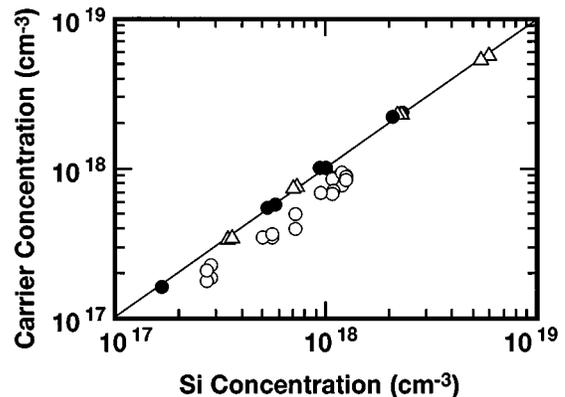


FIG. 5. Relation between carrier concentration and Si concentration in Si-doped GaAs by using Si₄ (●), by using Si₂H₆ (○), and Si-doped InP by using Si₄ (△).

etching with iodine (I) radicals. While carbon doping by CCl_4 promotes the etching of the grown layer at a high flow rate condition,¹² Si doping by SiI_4 eliminates this kind of problem due to a very low flow rate (high doping efficiency) and growth has been performed under a reduced SiI_4 flow rate. The growth rate for both GaAs InP did not change in spite of heavy doping due to the very low etching effect of the iodine, although a dependence of the alloy composition of $\text{In}_y\text{Ga}_{1-y}\text{P}$ on the flow rate of SiI_4 was observed at a higher doping level than $1 \times 10^{18} \text{ cm}^{-3}$. As the flow rate of SiI_4 increases from 5 to 10 sccm, the In composition in InGaP (y) decreases from 48.2 to 42.8% (becomes Ga rich). This phenomenon is similar to that of Jackson's *et al.* report⁹ which studied *n*-InGaAs by using SiBr_4 , and the consideration has to be discussed in more detail.

In conclusion, SiI_4 has been used as a new Si dopant source in GaAs and InP grown by CBE. The net carrier concentration of GaAs and InP doped by SiI_4 is comparable with previous reports using other dopants. A constant carrier concentration was obtained in a wide growth temperature range from 470 to 540 °C and a III/V ratio range from 10 to 20, so that an excellent sheet resistance of less than 2% uniformity for both *n*-GaAs and *n*-InP layers grown on 3 in. diameter was also obtained. The relation between carrier concentration and Si concentration in Si-doped GaAs by using SiI_4 and Si_2H_6 , and Si-doped InP by using SiI_4 was de-

termined and the electrical activation ratio of Si in SiI_4 for both GaAs and InP is almost 100% in the range studied, while that for Si_2H_6 is 80% or less. These satisfactory results suggest that SiI_4 is a promising candidate as a Si dopant source for CBE growth.

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