

# Si and C $\delta$ -doping of GaAs grown by metal organic vapour phase epitaxy for fabrication of nipi doping superlattices

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## Abstract

The growth conditions for Si and C  $\delta$ -doped nipi doping superlattices in GaAs have been optimised at the growth temperature of 630°C. We found that the Si  $\delta$ -doping concentration can be significantly changed by  $\delta$ -doping time over the range of  $10^{12}$ – $10^{13}$  cm<sup>-2</sup> at the optimised gas flow velocity. The similar range of the free hole density in C  $\delta$ -doped GaAs has also been obtained simply by varying the TMAI flow rate during the  $\delta$ -doping step. The full compensation of free electron and hole density in the Si and C  $\delta$ -doped nipsis can be achieved by choosing proper Si  $\delta$ -doping time and TMAI flow rate. Growth of one Si and C  $\delta$ -doped nipi in GaAs was demonstrated. Apart from the well-known effect of photo-excitation intensity on the effective band gap energy, the time-resolved photoluminescence reveals that the photoluminescence peak wavelength significantly increases in the relaxation process of the photo-excited nipi doping superlattice. © 1998 Elsevier Science S.A. All rights reserved.

**Keywords:**  $\delta$ -Doping; Nipi doping superlattices; MOVPE; Photoluminescence spectroscopy

## 1. Introduction

Nipi doping superlattice was first hypothesised in 1970 [1]. The unique charge transport-assisted optical and electro-optic nonlinear properties of the nipi have attracted increasing interest. Further investigation shows that  $\delta$ -doping instead of conventional bulk-doping in the nipsis can significantly improve their optical properties by diminishing the potential fluctuation in the growth direction [2,3]. In the  $\delta$ -doped nipi structures, the full compensation of n-type and p-type carriers is a great challenge to the growth techniques. Note that in metal organic vapour phase epitaxy (MOVPE), n-type and p-type  $\delta$ -doping are usually carried out at different temperatures due to the use of different doping precursors. This makes it extremely difficult to grow alternatively n-type and p-type  $\delta$ -doped structures with very thin undoped spacer layers, such as  $\delta$ -doped nipsis, at the same growth temperature. As a result, the  $\delta$ -doped nipi structures are normally grown in molecular beam epitaxy (MBE).

$\delta$ -Doping has recently been studied in MOVPE [4–6]. In this study, we present how to optimise Si  $\delta$ -doping in order to achieve a very high electron density at moderate temperatures. Combined with the use of a new C  $\delta$ -doping precursor, trimethylaluminium (TMAI), the growth of Si and C  $\delta$ -doped nipi doping superlattices is demonstrated. The results of photoluminescence study of one Si and C  $\delta$ -doped nipi are presented.

## 2. Experimental

MOVPE was used to grow Si and C  $\delta$ -doped layers in GaAs. The growth precursors were trimethylgallium (TMGa), and 100% AsH<sub>3</sub>. The doping precursors were trimethylaluminium (TMAI) and 500 ppm SiH<sub>4</sub> diluted in hydrogen. The reactor pressure and H<sub>2</sub> carrier gas flow rate were 76 Torr and 17.5 slm, however, during the Si  $\delta$ -doping step, the reactor pressure and H<sub>2</sub> carrier gas flow rate were changed to 400 Torr and 2 slm in order to increase the Si doping efficiency. Growth rate of GaAs was 2.6  $\mu\text{m h}^{-1}$  with a constant V/III ratio of 200. Epi-ready semi-insulating and n<sup>+</sup>

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$\langle 100 \rangle$  GaAs wafers oriented  $2^\circ$  off towards (110) were used as substrates. Detailed  $\delta$ -doping sequence has been described previously. [6] Briefly, the pre- $\delta$ -doping purge time was 10 s for C  $\delta$ -doping and 8 s for Si  $\delta$ -doping both with an  $\text{AsH}_3$  flow rate of 15 sccm. The  $\delta$ -doping time was 4 s for C  $\delta$ -doping without any  $\text{AsH}_3$  and variable for Si  $\delta$ -doping with an  $\text{AsH}_3$  flow rate of 160 sccm. No post- $\delta$ -doping purge step in Si  $\delta$ -doping but 4 s post- $\delta$ -doping purge step for C  $\delta$ -doping with an  $\text{AsH}_3$  flow rate of 35 sccm was employed.

### 3. Results and discussion

During the  $\delta$ -doping, the growth of host material is suspended by venting group IIIs in the ambience of  $\text{AsH}_3$ . Therefore,  $\delta$ -doping can be considered as the incorporation of dopants on the non-growing surface. At the growth temperatures normally used in MOVPE for GaAs,  $\text{SiH}_4$  molecules can not be completely decomposed into active Si doping species, i.e.  $\text{SiH}_2$ . It has been reported that the adsorption rate of the Si doping species on the surface can be increased by enhancing the thermal decomposition efficiency of  $\text{SiH}_4$  at elevated growth temperatures and/or increasing the partial pressure of  $\text{SiH}_4$  in the gas phase [7]. Our previous study shows that the electron density is also very sensitive to the gas flow velocity [8]. The optimised gas flow velocity under our growth conditions has been found, which corresponds to the  $\text{H}_2$  carrier gas flow rate of 2 slm at the reactor pressure of 400 Torr. In this work, the electron density of Si  $\delta$ -doped GaAs was changed by only varying Si  $\delta$ -dop-

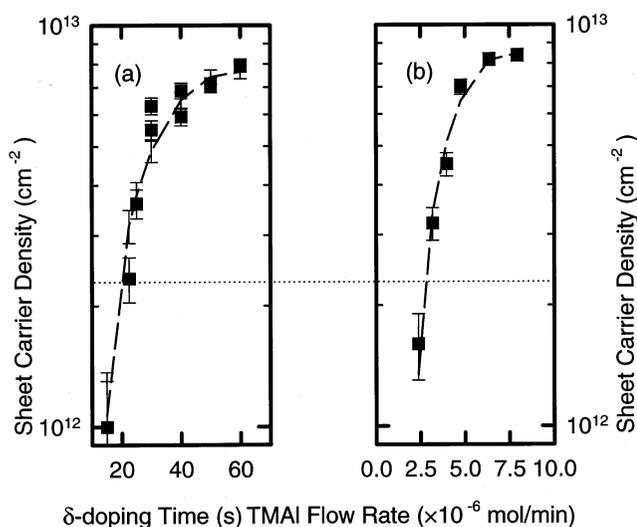


Fig. 1. (a) The dependencies of the sheet electron density of Si  $\delta$ -doped GaAs on  $\delta$ -doping time at the given  $\text{SiH}_4$  flow rate of  $4.35 \times 10^{-7} \text{ mol min}^{-1}$ , and (b) the sheet hole density of C  $\delta$ -doped GaAs on TMAI flow rate.

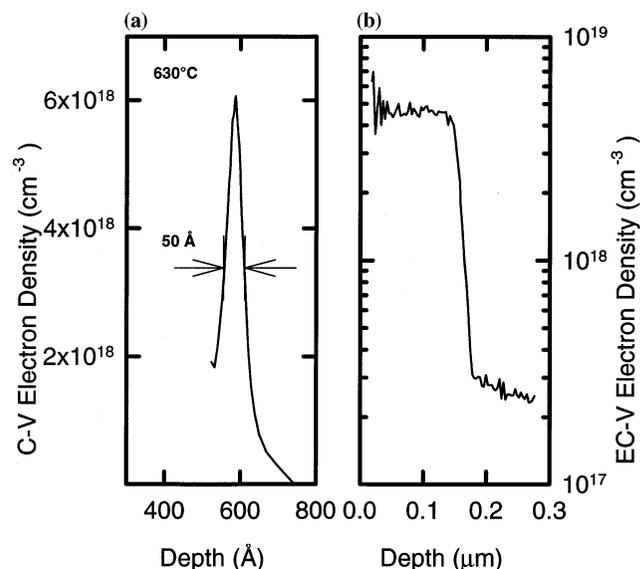


Fig. 2. The electron profiles of a single Si  $\delta$ -doped layer in GaAs (a) and a multiple Si  $\delta$ -doped nini doping superlattice in GaAs (b). Both of them were grown at  $630^\circ\text{C}$ . The growth parameters included the  $\delta$ -doping time: 30 s, the  $\text{SiH}_4$  flow rate:  $4.35 \times 10^{-7} \text{ mol min}^{-1}$ , the  $\text{H}_2$  flow rate: 2 slm. The undoped spacer layer thickness in the Si  $\delta$ -doped nini doping superlattices was 100 Å.

ing time under those optimised growth conditions at  $630^\circ\text{C}$ . The results shown in Fig. 1(a) indicate that the electron density can be varied from  $1 \times 10^{12}$  to  $\sim 8 \times 10^{12} \text{ cm}^{-2}$ . At  $630^\circ\text{C}$ , the thermal diffusion of Si dopants in GaAs is weak [6]. So even using a relatively long  $\delta$ -doping time, for example 30 s, the out-diffusion of the Si dopants from the  $\delta$ -doped layer can be neglected. The electron profiles of one Si  $\delta$ -doped layer in GaAs and Si  $\delta$ -doped nini doping superlattice in GaAs are shown in Fig. 2. The achieved peak electron density is  $> 6 \times 10^{18} \text{ cm}^{-3}$ .

Trimethylaluminium (TMAI) has been used as an efficient C  $\delta$ -doping precursor in MOVPE [5]. It was reported that the free hole density of C  $\delta$ -doped GaAs is insensitive to the change of growth temperature over the region of  $550$ – $670^\circ\text{C}$ . It is required to grow Si and C  $\delta$ -doped layers in the nipi structure at the same growth temperature. The free hole density of C  $\delta$ -doped GaAs is therefore calibrated at  $630^\circ\text{C}$ . Fig. 1(b) shows that by varying the TMAI flow rate at the fixed  $\delta$ -doping time of 4 s, the free hole density can be changed over the region of  $1 \times 10^{12}$ – $8.5 \times 10^{12} \text{ cm}^{-2}$ , which covers the similar region of the free electron density in Si  $\delta$ -doped GaAs, see Fig. 1(a). The corresponding TMAI flow rate and the Si  $\delta$ -doping time was decided in Fig. 1 (see the vertical line in Fig. 1) to grow Si and C  $\delta$ -doped nipi in GaAs. The sheet carrier density of each Si and C  $\delta$ -doped layers were aimed to be  $2.3 \times 10^{12} \text{ cm}^{-2}$ . The nipi was then characterised electrically using electro-chemical capacitance–voltage profiler (EC–V) and optically using photoluminescence spectroscopy.

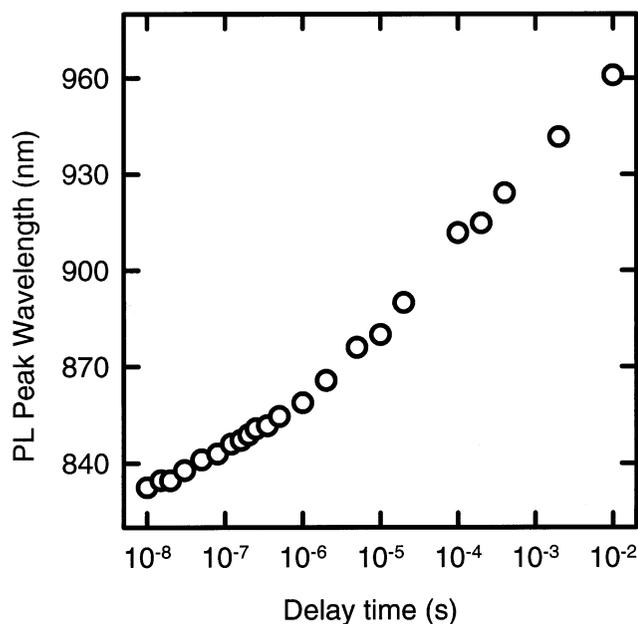


Fig. 3. The photoluminescence peak wavelength of the photo-excited Si and C  $\delta$ -doped nipi in GaAs as a function of delay time.

The EC-V profiling shows that the carrier density over the Si and C  $\delta$ -doped nipi region was even lower than the background ( $< 1 \times 10^{16} \text{ cm}^{-3}$ ) of undoped GaAs. This implies that the full compensation of Si and C  $\delta$ -doped layers in the free carrier density has been achieved. One unique property of nipi is that its effective band gap can be tuned by illumination, leading to the shift of photoluminescence (PL) peak energy with the photo-excitation power. We found that when the photo-excitation power was changed from 10 to  $10^{-5} \text{ mW mm}^{-1}$ , the PL peak energy shifts by about 200 meV. So, the quality of our MOVPE-grown Si and C  $\delta$ -doped nipi is comparable to the best grown in MBE. It is further prospected that those MOVPE-grown Si and C  $\delta$ -doped nipsis can be used in quantum well structures, also known as hetero-nipi for device applications [9].

The time-resolved PL has also been used to probe the emission wavelength of the Si and C  $\delta$ -doped nipi as a function of delay time. It can be seen in Fig. 3 that the emission wavelength significantly increases from 830 to 961 nm over the delay time region of  $10^{-8}$ – $10^{-2}$  s. In

other words, after a pulsed photo-excitation, the nipi structure emits photons with different energies at different delay times. The whole process represents the relaxation of the photo-excited internal saw-tooth-shaped electrical field. This relaxation process involves recombination of photo-excited electrons with holes. A more detailed study of optical properties of Si and C  $\delta$ -doped nipsis will be published elsewhere.

#### 4. Conclusion

The growth conditions of Si and C  $\delta$ -doped layers in GaAs have been optimised in MOVPE at 630°C. The free electron density and free hole density of Si and C  $\delta$ -doped layers can be changed from  $10^{12}$  to  $\sim 10^{13} \text{ cm}^{-2}$  simply by changing the Si  $\delta$ -doping time and the TMAI flow rate, respectively. By choosing proper Si  $\delta$ -doping time and TMAI flow rate, the full compensation of free carrier density in Si and C  $\delta$ -doped nipi has been demonstrated in MOVPE-grown structures. The quality of MOVPE-grown Si and C  $\delta$ -doped nipsis in GaAs was assessed using electrical and optical techniques. The relaxation of the nipi effective bandgap after a pulsed photo-excitation induces dependence of the PL peak wavelength on the delay time.

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