Photoluminescence study of the incorporation of silicon in GaAs grown by molecular beam epitaxy

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The effect of substrate temperature and As/Ga flux ratio on the incorporation of Si as a dopant in GaAs grown by molecular beam epitaxy has been studied by means of low-temperature photoluminescence (PL) measurements. It is shown that the acceptor character of Si is enhanced as the substrate temperature increases from 590 to 720 °C. The PL results suggest that the amount of Si self-compensation decreases when the atomic flux ratio increases from 2 to 6.

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Silicon and tin are the dopants most frequently used to obtain n-type layers of GaAs grown by molecular beam epitaxy (MBE). Being group IV elements, both could in principle show amphoteric behavior but Sn seems to exhibit self-compensation to a much smaller extent. However, due to its segregation, Sn is seldom used in device applications.

The dominant character of Si as an acceptor has been demonstrated in layers grown by liquid phase epitaxy[1] (LPE) when grown below a critical temperature (~ 900 °C). On the other hand, no evidence of Si acceptors has been found in vapor phase epitaxy (VPE) GaAs, where, for standard growth temperatures (~ 750 °C), the ratio of the As to the Ga fluxes is large and, based on thermodynamic arguments, the number of Si donors should be at least three orders of magnitude greater than that of Si acceptors.[2] In MBE GaAs, however, both Ga and As-rich growth conditions can be obtained at typical substrate temperatures (~ 600 °C). Under moderately As-rich conditions, which yields high-quality films, Si acts primarily as a donor, although there is some evidence of its amphoteric character under different growth conditions.[3-7]

In this communication we report a study of the effect of As/Ga flux ratio and substrate temperature, T_G, on the incorporation of Si in MBE-grown GaAs, based on photoluminescence (PL) measurements. Our results indicate that for a given T_G the amount of Si self-compensation decreases with increasing flux ratio, and increases as T_G is increased, which leads to a largely self-compensated GaAs grown at ~ 700 °C. This is significant because many electronic and optoelectronic devices are based on thin GaAs–$Ga_{1-x}Al_xAs$ heterostructures, grown at $T_G \sim 700$ °C, which is necessary for high-quality $Ga_{1-x}Al_xAs$.

The GaAs layers were prepared by MBE on (001) Cr-doped substrates using a procedure described earlier.[8] The epilayers consisted of a 0.2-1 μm thick undoped GaAs buffer layer, followed by a 2-5 μm of Si-doped GaAs, at temperatures in the range 590–720 °C. Unless otherwise specified, the atomic flux ratio of As to Ga for samples grown at 590 °C was ~ 5. For layers grown at or above 630 °C the ratio was increased to ~ 10 to obtain mirror-like surface morphology.

Carrier concentration n and mobility μ at 300 and 77 K, were determined from Hall effect measurements using van der Pauw configurations. Table I summarizes the results for lightly doped samples grown at various substrate temperatures under a constant Si flux. As T_G is increased, a decrease in the number of carriers is observed, indicating an increasing compensation of the donors by acceptors. In addition, a monotonic decrease in the mobility occurs as T_G increases, possibly due to an overall degradation of the GaAs quality. The sample grown at 720 °C had high resistance and Hall measurements were not possible; this is probably a consequence of low carrier concentration, which leads to a full depletion of the grown epilayer.

Luminescence measurements, done on the samples of Table I, have confirmed the existence of donor compensation and have identified Si as the increasingly compensating element, as T_G is increased. The experiments were carried out by exciting the GaAs epilayers, placed in a cryostat, with the 5145 Å line of an Ar^+ laser. The induced luminescence was detected with a photomultiplier equipped with a cooled

TABLE I. Number of carries n, and mobility μ, at 300 and 77 K, for samples grown at different temperatures under varying As/Ga fluxes.

T_G (°C)	As/Ga (relative)	n_{300} (10^{15} cm^{-3})	μ_{300} (10^3 cm^2/V · s)	n_{77} (10^{15} cm^{-3})	μ_{77} (10^3 cm^2/V · s)
590	1	1.2	7.34	1.1	39.3
630	1.8	0.56	6.96	0.47	29.0
680	1.8	0.47	6.73	0.39	26.2
700	1.9	0.35	6.36	not ohmic	not ohmic
720	1.9	...	...	...	...

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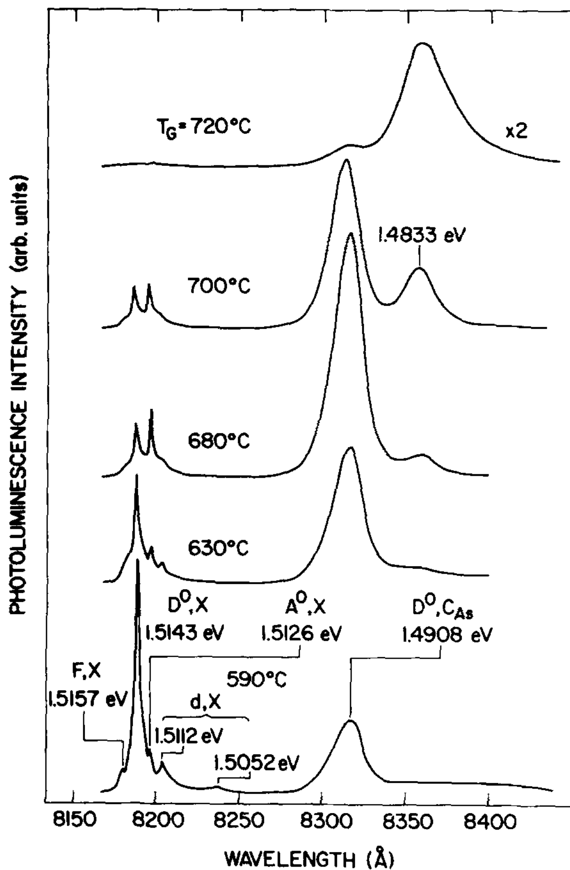

FIG. 1. Low-temperature PL spectra of various Si-doped GaAs epilayers grown at different temperatures. The Si flux during growth was the same for all the samples but the As/Ga flux ratio was varied (see Table I). The intensity scale is the same for all the spectra except for the one with $T_G = 720$ °C, as indicated.

was detected with a photomultiplier equipped with a cooled GaAs cathode placed at the exit slit of a double-pass 0.75-m spectrometer. The results for low-intensity excitation (~ 0.2 W/cm^2) and low-temperature ($T \leqslant 2$ K) are summarized in Fig. 1. The spectra show structures in two distinct regions: one between 8175 and 8250 Å, associated with excitonic transitions, and another between 8275 and 8450 Å, related to transitions involving acceptor states.

For the sample grown at $T_G = 590$ °C, the structures observed in the short-wavelength region are indicative of very high-quality GaAs,[7–9]: a free exciton (F, X), an exciton bound to Si acting as a donor ($D°, X$), and an exciton bound to the acceptor carbon ($A°, X$), invariably present in MBE-grown GaAs. Two additional peaks at 1.5112 and 1.5052 eV have been attributed[6,7] to defect bound excitons (d, X). As Fig. 1 shows, the 1.5052-eV exciton peak disappears at $T_G \gtrsim 630$ °C, in agreement with the observation of Künzel and Ploog,[6] who attributed it to the growth mechanisms. On the other hand, the intensity of the other defect-related peak, at 1.5112 eV, decreases with increasing T_G but can still be traced at 700 °C. Also, as T_G increases, the intensity of the ($D°, X$) peak, relative to the ($A°, X$) peak, decreases and suggests a decrease in the number of donors.

The structure at 1.4908 eV, for $T_G = 590$ °C, is interpreted as resulting from the carrier recombination between Si donor and C acceptor states. The increase in intensity of this peak, along with the ($A°, X$) structure, as T_G increases up to 680 °C, is probably indicative of an increase in the overall PL efficiency.[6] However, if T_G is too high, an excessive number of vacancies, acting as nonradiative centers, may overshadow that effect, as supported by the results for samples grown above 680 °C, shown in Fig 1.

The most salient feature in the long-wavelength region of the spectra of Fig. 1 is the appearance of a new peak at 1.4833 eV when $T_G \approx 630$ °C, whose intensity increases monotonically with T_G. We attribute the peak at 1.4833 eV to the Si donor to Si acceptor transition, ($Si°_{Ga}$, $Si°_{As}$). This transition has been observed in LPE GaAs,[1] at slightly lower energy; the small discrepancy is most likely due to the $e^2/\epsilon r$ term involved in the transition energy of a donor–acceptor (D–A) transition.[10] (ϵ is the static dielectric constant and r is the D–A separation, which depends on doping concentration, temperature and excitation intensity.)

We have confirmed our ascription from PL measurements under various excitation intensities, shown in Fig. 2. As the excitation power density is increased from 0.1–25 W/cm^2, a slight shift of the 1.4833-eV peak toward higher energies is observed. This upshift, characteristic of D–A transitions, results from the saturation of distant pairs that effectively reduces r.[10] At the highest excitation, the peak energy of 1.4860 eV represents the conduction band to Si acceptor (e, $Si°_{As}$) transition. The discrepancy of ~ 1 meV with the

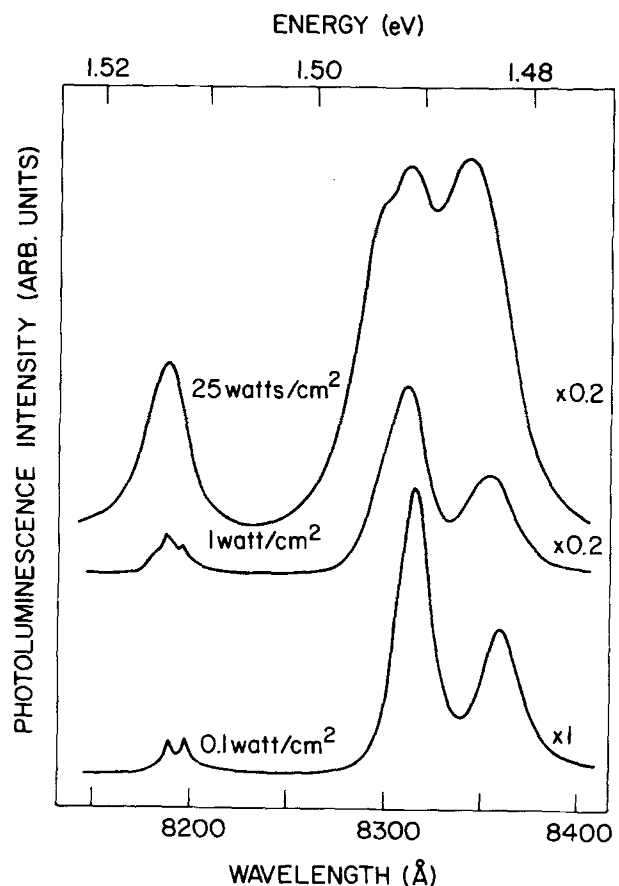

FIG. 2. PL spectra of GaAs grown at 700 °C for different excitation intensities.

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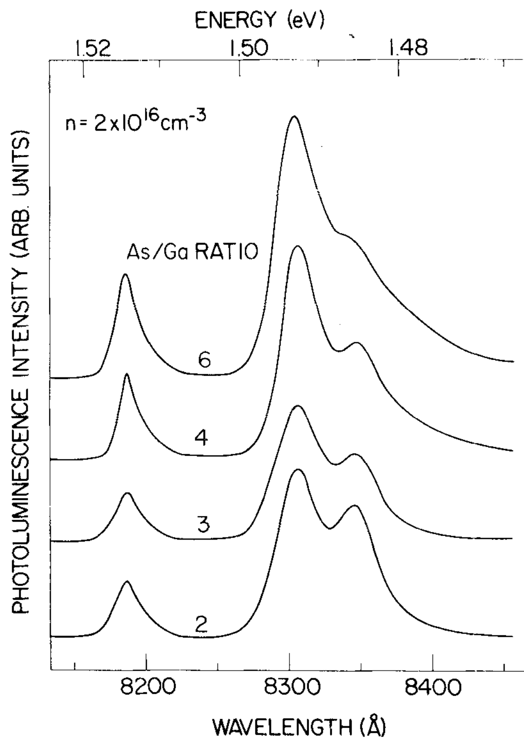

FIG. 3. PL spectra of Si-doped GaAs, grown at 590 °C, for different atomic As/Ga flux ratios.

value reported by Ashen *et al.*[2] is within the spread from sample to sample, especially when, as in our case, the (Si°_{Ga}, Si°_{As}) and (e, Si°_{As}) peaks merge with each other and with the peaks involving C. For excitations as large as 25 W/cm^2 the carbon related structure can be separated into two: (e,C°_{As}) at 1.4938 eV and (Si°_{Ga}, C°_{As}) at 1.4914 eV.

The increase in intensity of the Si acceptor peak as T_G increases, observed in Fig. 1, indicates an increase in the number of As vacancies, which in turn are filled with Si atoms and act as acceptors. In principle, the number of these vacancies may be reduced by increasing the As flux relative to the Ga flux during the growth of the GaAs epilayer. To check this possibility, four Si-doped layers, each 1 μm thick, were grown sequentially one on top of the other. The Si flux was kept constant throughout the entire growth but the As/Ga flux was varied from layer to layer between ~ 2 and 6. The average carrier density, as obtained from Hall measurements, was $2\times 10^{16}cm^{-3}$. The sample was then selectively etched to a determined depth, to expose different layers.

PL spectra of the various layers, taken at ~ 2 K under low-intensity excitation, are plotted in Fig. 3 using the same scale, shifted vertically. No major variation of the integrated PL intensity is observed with flux ratio, but the Si acceptor peak (1.485 eV) decreases in intensity relative to the C acceptor peak (1.4926 eV), as the flux ratio is increased, suggesting a reduction in the number of As vacancies. On the other hand, C–V measurements performed on these layered structures revealed surprisingly that the carrier concentration does not increase monotonically with the flux ratio, but reaches a maximum at some intermediate flux between 3 and 4. This apparent contradiction with the PL results is being investigated.

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