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2002 Phys. Scr. 2002 114

(http://iopscience.iop.org/1402-4896/2002/T101/030)

Physica Scripta. T101, 114–118, 2002

Potential Fluctuations and Site Switching in Si-doped GaAs Studied by Photoluminescence

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Received June 13, 2001; accepted October 15, 2001

PACS Ref: 73.61.Ey, 78.55.Cr

Abstract

We report on a photoluminescence (PL) study of highly compensated Si-doped GaAs. Si-doped GaAs layers were grown p-type at 700°C by liquid phase epitaxy and subsequently converted to n-type by thermal annealing at temperatures above a transition temperature of about 840°C. Annealing at temperatures close to the transition temperature resulted in a very high degree of compensation. This is verified by a large shift of photoluminescence bands with excitation intensity, up to 24 meV per decade of increase in the excitation power density. We attribute the shift to the presence of potential fluctuations which we correlate with a possible site-switching of Si from Ga sites to As sites. Our results strongly suggest that the type conversion from p- to n-type is in fact caused by site-switching of the Si impurity.

1. Introduction

The amphoteric nature of the Si impurity in GaAs is a well known fact. Substitutional group IV impurities in III-V semiconductors, such as Sn, Ge, or Si in GaAs, may occupy gallium sites where they behave as shallow donors, or arsenic sites where they are shallow acceptors. In particular, Si is known to behave amphoterically in GaAs [1]. For low total Si concentrations the solubility of Si donors occupying Ga lattice sites (Si_{Ga}) is greater than the solubility of Si acceptors occupying As lattice sites (Si_{As}). At very high Si concentrations a severe self compensation occurs [2]. When the total concentration of Si in GaAs exceeds $10^{18}\,cm^{-3}$ defect interactions become more complicated and we observe various kinds of interstitial or interstitial-substitutional complexes [3].

Ashwin *et al*. [4] and Spitzer *et al*. [5,6] found that at high growth temperatures Si-doped GaAs grown by liquid-phase-epitaxy (LPE) is n-type but highly compensated, while at lower growth temperatures it is compensated and p-type. The actual crossover point depends on temperature, silicon concentration and crystal orientation [7]. At low doping levels the carrier concentration tends to rise linearly with the total Si concentration $[Si]_{tot}$. Auto-compensation causes problem at high doping levels although carrier concentrations as high as $\sim 10^{20}\,cm^{-3}$ have been achieved by low temperature growth (300–600°C) [1].

A site-switching of silicon on arsenic site Si_{As} to form silicon on gallium site Si_{Ga} in As ambient gas may be formulated as follows:

$$\begin{array}{ll} & Si_{As} + V_{Ga} \rightleftharpoons Si_{Ga} + V_{As} \\ + & As(g) + V_{As} \rightleftharpoons As_{As} \\ \hline & As(g) + Si_{As} + V_{Ga} \rightleftharpoons Si_{Ga} + As_{As} \end{array} \qquad (1)$$

The Si_{Ga} is usually considered more mobile than Si_{As} [2] but at high temperatures (>840°C) the kinetics favor Si on Ga site. By looking at Eq. (1), one would except the reaction to be driven to the right by increasing the ambient As(g) pressure, thereby aiming for a higher concentration of Si on Ga sites, Si_{Ga}. Arsenic could also occupy the gallium vacancies but its affinity for arsenic vacancies is significantly higher. Gallium arsenide grown by LPE from gallium melt is expected to be low in gallium vacancy defects and possibly high in arsenic vacancies [8]. If GaAs is solution grown from gallium under conditions where there are few gallium vacancies, Si is a shallow acceptor.

The *degree* of compensation η is often defined as [9]

$$\eta = \frac{N_D^+ + N_A^-}{n} \qquad (2)$$

where n is the free electron concentration ($\simeq N_D^+ - N_A^-$) in n-type material. N_D^+ and N_A^- denote the concentration of ionized donors and acceptors, respectively. Similar equation is also valid for p-type material if n is replaced by $p = N_A^- - N_D^+$. An alternate approach is to define the compensation *ratio* as N_A^-/N_D^+ [9] for n-type but N_D^+/N_A^- in the case of p-type material.

By annealing p-type samples at temperatures around the transition temperature, they are converted to a highly compensated state and to n-type samples at still higher temperatures. Furthermore, the compensation degree can be varied with the annealing temperature, peaking to infinity at the transition temperature. In a review article by Newman [1] the lattice locations of silicon impurities in GaAs are summarized. Furthermore, they are related to the electrical properties of n-type Bridgman, liquid-encapsulated Czochralski (LEC), molecular beam epitaxial (MBE) (001) GaAs on the one hand, and to p-type liquid phase epitaxial and MBE (111) A layers on the other hand. Newman focused on highly doped n-type material and its saturation above 5×10^{18}–$10^{19}\,cm^{-3}$, depending on the type of GaAs material. In the present investigation we study the highly compensated regime of GaAs:Si and potential fluctuations caused by the reduction of Coulombic screening in the material.

Highly compensated semiconductors are known to exhibit potential fluctuations as a result of insufficient screening of ionized impurities by free carriers [10]. In photoluminescence (PL) measurements potential fluctuations are manifested by a downward shift in photon energy of the near bandgap PL bands through localization of the charge carriers, as well as a shift of the localized PL bands to higher energy with increasing excitation power density. This shift is much larger than that of donor-to-acceptor pair (DAP) bands with excitation intensity. Furthermore, in contrast to ordinary DAP recombination, the bands shift to lower energy at higher temperatures.

In GaAs such fluctuations have been studied by photoluminescence in Li-compensated material [11] and in highly Ge-doped material [12]. Here we report on photoluminescence measurements of potential fluctuations in Si-doped GaAs, which has been converted from as-grown p-type to n-type by annealing above the transition temperature.

2. Sample preparation

A roughly 1 μm thick GaAs film was grown by liquid phase epitaxy on a semi-insulating (SI) GaAs (100) substrate. The substrate was brought into contact with liquid Ga metal of purity 6N at 700°C, saturated with As and containing dissolved Si. By lowering the temperature the solution becomes supersaturated with respect to As and the film growth nucleates at the substrate. The growth process took place in reducing H_2 ambient of purity 7N and in graphite crucibles. For this study two LPE batches were made, differing in the amount of Si in the growth solutions. While all other growth conditions were kept the same the Si/Ga mass ratio in the growth solutions was altered from 1.2×10^{-4} to 2.1×10^{-3} ($\simeq 3.0 \times 10^{-4}$ and 5.2×10^{-3} mole fraction, respectively). According to [8] this should correspond to a net hole concentration $\sim 3 \times 10^{17}$ and $\sim 5 \times 10^{8}\,\mathrm{cm}^{-3}$, respectively, in as-grown GaAs.

Si-doped GaAs grown by LPE is highly compensated for growth temperatures around 840°C. It is n-type and still quite compensated if grown at higher temperatures but p-type if grown at lower temperatures. Pieces of the two as-grown LPE batches were baked in quartz ampoules at 840°C for 24 h with a subsequent quenching in liquid nitrogen. To retard V_{As} formation during baking a small amount of As(s) was put into the ampoule prior to evacuation. The ampoules were closed at 1.0×10^{-5} mb pressure. Arsenic sublimates at 613°C. The amount of As in the ampoule was controlled to a given As(g) pressure slightly bellow 1 bar at the baking temperature.

3. Experiment

The free carrier concentration was obtained by Hall measurements. Using square samples, ohmic contacts were welded on the four corners with tin- or zinc-coated gold wire, tin in the case of n-type samples and zinc in the case of p-type samples. The ohmic contacts were made so to avoid heating while alloying the contacts. A typical sample size was $3 \times 3\,\mathrm{mm}^2$. The Hall coefficient R_H was estimated from the slope of the Hall voltage vs. the magnetic field in the range of 0–0.5 Tesla, Tesla, and an average of four values in each point was calculated where the two pairs of contacts were interchanged and the current reversed. Electron and hole concentrations were calculated from the Hall coefficient R_H as $n = -r_H/eR_H$ and $p = r_H/eR_H$, respectively, assuming the Hall scattering factor r_H to be isotropic, temperature independent and of unit value ($r_H \equiv 1$).

Photoluminescence measurements were performed at 14 K using a closed-cycle He cryostat. The 532 nm line of a Verdi Nd:YVO4 laser from Coherent was used as an excitation source. The excitation intensity was varied over several decades and the PL signal was detected via a double 0.85 m Spex 1404 grating monochromator using a cooled Ge detector. The spectra presented here were not corrected for the spectral response of the instruments. Hall measurements were performed to determine the majority carrier type. The nominator term in equation (2), $N_D^+ + N_A^-$, is assumed to be identical to the total concentration of silicon, $[\mathrm{Si}]_{tot}$ at room temperature whilst the denominator term is approximated by the free carrier concentration observed by the Hall measurements.

4. Experimental results

Two GaAs samples were grown p-type under the conditions described above. One was grown with a low Si concentration (Sample #1), $p = 1.6 \times 10^{17}\,\mathrm{cm}^{-3}$, and the other with a higher Si concentration (sample #2), $p = 4.0 \times 10^{18}\,\mathrm{cm}^{-3}$Annealing converted both samples to n-type with rather similar electron concentration, sample #1a with $n = 3.9 \times 10^{17}\,\mathrm{cm}^{-3}$ and sample #2a with $n = 3.8 \times 10^{17}\,\mathrm{cm}^{-3}$. We note that in addition to the type conversion there is a significant difference in the compensation degree of sample #2 before and after annealing, since the net electron concentration in sample #2a is only about 10% of the original hole concentration. In the less Si-doped sample #1 the carrier concentration before and after annealing remains the same within a factor of two. Table I summarizes the carrier concentration of each sample.

As-grown, unintentionally doped GaAs exhibits bound exciton (BE) spectra around 1.51 eV and donor-acceptor (DAP) pair spectra which merge with free-to-bound (FB) around 1.49 eV when the donors become ionized. In lightly Si-doped samples the Si-donor to Si-acceptor pair band peaks at 1.482 eV at low temperatures, and the FB transition around 1.485 eV [13]. The band-edge PL bands are not observed on the intensity scale of Fig. 1(a), which shows the photoluminescence spectrum of the as-grown sample #1 with low Si concentration. Instead the spectrum is dominated by a broad PL band peaking around 1.445 eV at an excitation intensity level of 0.001 W.

The laser beam was focused to an area of $\sim 1\,\mathrm{mm}^2$. For each series of excitation intensities the area was kept constant. Increasing the excitation intensity of sample 1# by two orders of magnitude to 0.1 W shifts the peak position around 6 meV per decade of change in excitation intensity. In the discussion section we interpret this shift in terms of the presence of potential fluctuations caused by insufficient screening of ionized impurities. Annealing at 840°C dramatically changes the spectrum as shown in Fig. 1(b) (sample #1a). The intensity is much weaker as

Table I. *The carrier concentration in as grown and annealed samples obtained by Hall measurements and PL peak shift with excitation intensity in as grown and annealed samples measured at 14 K.*

Sample	Carrier concentration [cm^{-3}]	Shift [meV/decade]
#1	$p = 1.6 \times 10^{17}$	6 meV
#1a	$n = 3.9 \times 10^{17}$	5 meV
#2	$p = 4.0 \times 10^{18}$	5 meV
#2a	$n = 3.8 \times 10^{17}$	24 meV

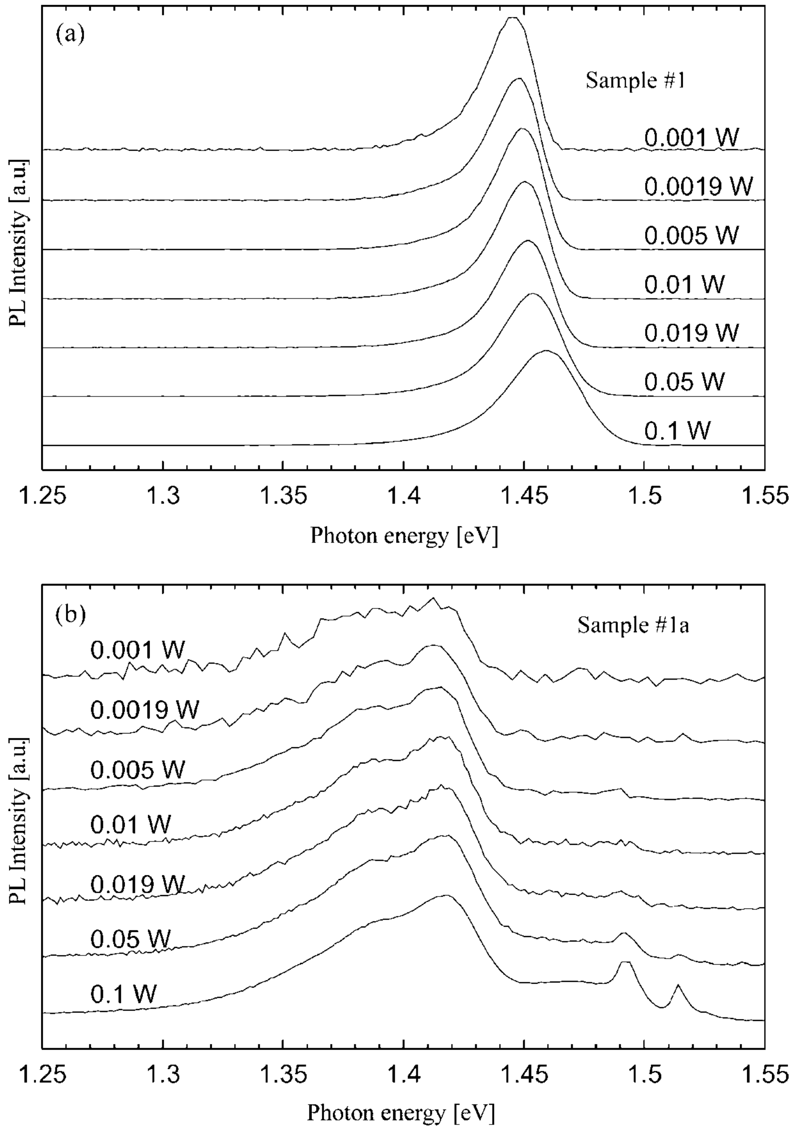

Fig. 1. Peak shift with excitation intensity of a PL band measured at 14 K in (a) as-grown p-type LPE sample grown to have low Si concentration and (b) the same sample n-type after annealing at 840°C for 24 h.

evidenced by the presence of the band-edge PL bands from unperturbed regions of the sample. These PL bands only shift insignificantly with excitation intensity, the DA pairs typically shifting less than 1 meV per decade. The main PL band peaking around 1.42 eV also shows a negligible shift with excitation intensity, thus originating from unperturbed regions of the sample. We attribute this band to defect-related transitions induced by the annealing. Another weaker band at 1.385 eV for the lowest excitation intensity shows a shift around 5 meV per decade of change in intensity. Hence, this band is an evidence for the presence of potential fluctuations after annealing.

Fig. 2(a) shows the photoluminescence spectrum of the as-grown sample #2 with high Si concentration. The spectrum exhibits a broad, strong peak at 1.435 eV for an excitation level of 0.001 W. This peak shows a similar shift with excitation intensity as sample #1, about 5 meV per decade of change. In this sample the annealing produces a strong shift in the PL spectrum as illustrated in Fig. 2(b). A broad peak around 1.35 eV at 0.001 W shifts some 24 meV per decade of change in excitation intensity. In addition, the spectrum shows the usual band-edge luminescence.

Figure 3 summarises the dependence of the peak positions of the as-grown and annealed samples on the excitation intensity. Table I lists the observed shift rate of the PL bands in addition to the carrier concentration of each sample.

5. Discussion

In highly compensated semiconductors the fixed charge may be randomly distributed. Donor- and acceptor-rich regions may appear locally and, hence, positively and negatively charged domains. Under normal circumstances such fluctuations in the local potential are screened by mobile carriers, while at high compensation degree the screening is insufficient. Radiative recombination in the depleted regions can be described as taking place between carriers confined to spatially separated potential wells which originate from fluctuations in the distribution of charged impurities [10,11].

The localization lowers the photon energy of donor-to-acceptor pair transitions by twice the potential well depth or

$$h\nu = E_g - (E_D + E_A) - 2\gamma(r_s) \quad (3)$$

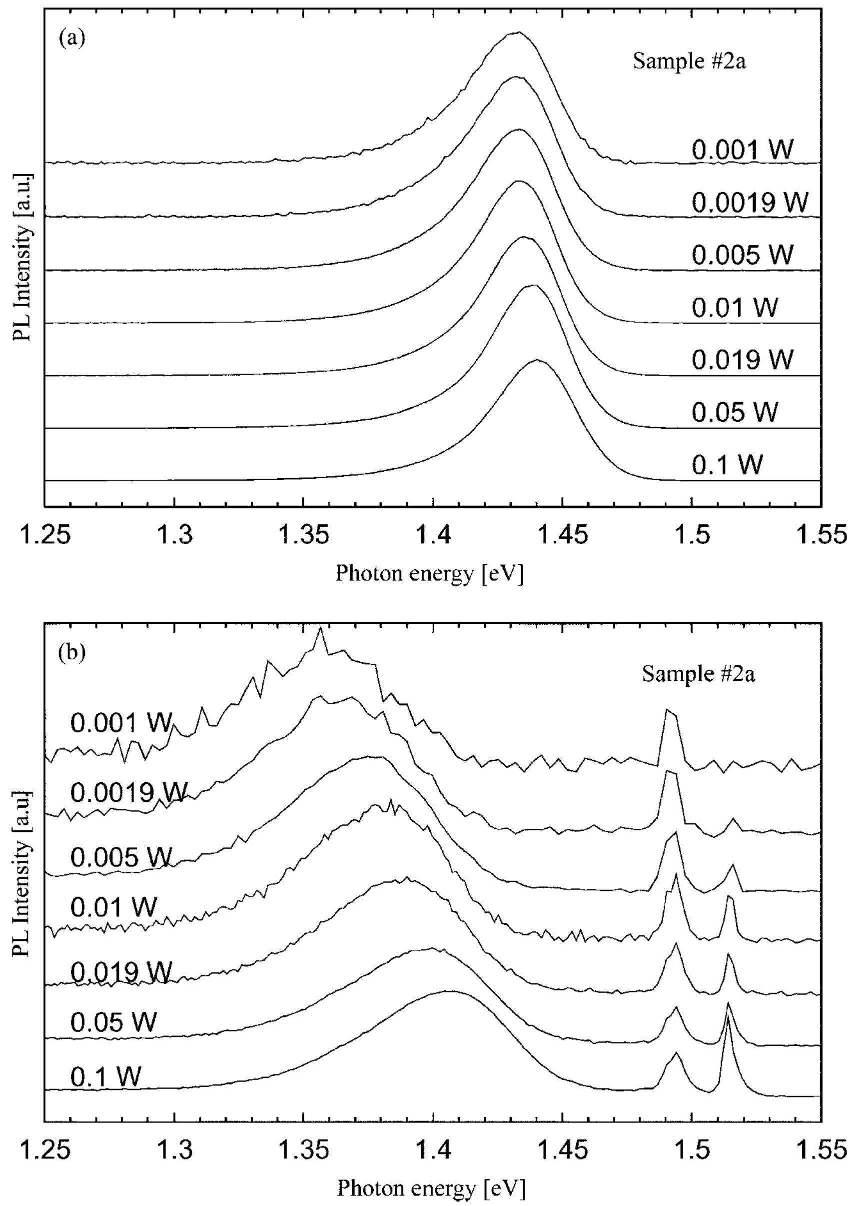

Fig. 2. Peak shift with excitation intensity of a PL band measured at 14 K in (a) an as-grown p-type LPE sample grown to have low Si concentration and (b) the same sample n-type after annealing at 840°C for 24 h.

where E_g is the band gap energy, E_D the ionization energy of the donor and E_A the ionization energy of the acceptor. The potential well depth is

$$\gamma(r_s) = \frac{e^2}{4\pi\epsilon_0\epsilon_r r_s}(N_t r_s^3)^{1/2} = \frac{e^2}{4\pi\epsilon_0\epsilon_r}\frac{N_t^{2/3}}{n^{1/3}} \tag{4}$$

where N_t the total concentration of charged impurities in the material and r_s is the screening radius defined as $r_s = N_t^{1/3}/n^{2/3}$ in the case of n-type semiconductors. The impurities are assumed to have Gaussian distribution.

From Eqs (3) and (4) we see that the well depth increases with increasing concentration of charged impurities N_t but decreases with increasing concentration of free charge carriers. From the equations one expects a PL band in the presence of potential fluctuations to shift to lowest photon energy in highly compensated semiconductors which originally had high shallow doping. Also one expects a shift to higher energies with increased excitation intensity which increases the concentration of photoexcited carriers. This is indeed what we observe.

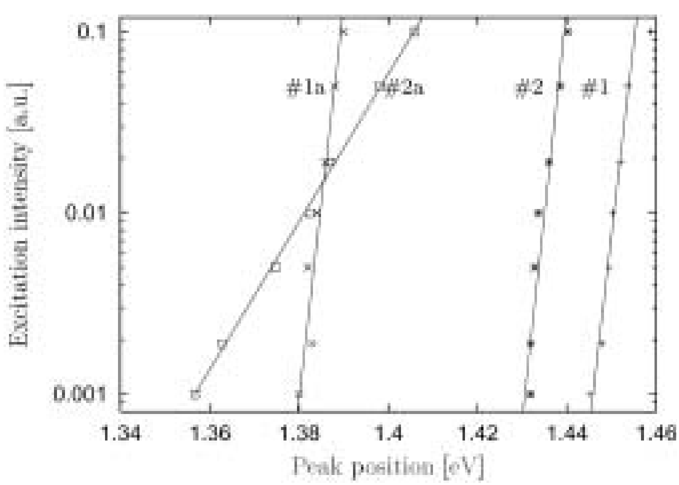

Fig. 3. PL peak position for different excitation intensities for the four samples. The slope of each curve represents the shift rate with excitation intensity.

In the present work we emphasize the two ways in which compensation can be obtained in Si-doped GaAs. The obvious one is direct growth under conditions which ensure close compensation of Si_{Ga} donors by Si_{As} acceptors. We have accomplished such doping as evidenced by the presence of shifting PL bands in the as-grown samples. Comparing the as-grown spectra of the two samples #1 and #2 in Fig. 3 we note that the shift rate with excitation intensity is comparable for both samples while the peak position is somewhat lower in energy for sample #2 which has a higher Si_{tot} concentration. This is in a general agreement with the higher concentration of ionized impurities according to Eq. (3), although the higher concentration of free carriers in sample #2 reduces the corresponding well depth.

The type conversion from p-type to n-type through annealing also illustrates a way of obtaining a striking range of compensation degree. A significant difference between the two samples is evident upon annealing as shown in Fig. 3. The highly doped sample #2a shows a substantial shift whereas the shift rate of the weakly doped sample remains low. Note that the PL and around 1.42 eV in sample #1a in Fig. 1(a) is not a shifting PL band, while the shoulder on the high energy wing of that band indicates potential fluctuations. This difference can again be accounted for by Eq. (3). Although the electron concentration of the two samples after annealing is rather similar, the large shift of the PL band in sample #2a is typical of a strong concentration of highly compensated ionized impurities. The PL shift accompanies a reduction of the free carrier concentration by a factor of ten in addition to the type conversion. The measured Hall concentration in the as-grown sample #2 can therefore be concluded to reflect the lowest possible Si_{As} concentration and a low compensation degree η, whereas the Si_{Ga} and Si_{As} concentrations become roughly similar upon annealing, with a high compensation degree as a consequence. Due to the high As(g) concentration during annealing one might expect, to some extent, the formation of the deep donor As_{Ga} although we assume its concentration to be negligible compared to the measured carrier concentration.

6. Conclusion

Annealing at temperatures close to a transition temperature of 840°C resulted in a very high compensation ratio as verified by a large shift of localized PL bands with excitation intensity. The presence of potential fluctuations is manifested through a shift of the PL peak position of up 24 meV per decade of increase in the excitation power density. We have correlated the observation of potential fluctuations with a possible site-switching of Si from Ga sites to As sites. Our results strongly suggest that the type conversion from p- to n-type to is in fact caused by such site switching.

Acknowledgements

This work was partially supported by the Icelandic Research Council and The University of Iceland Research Fund.

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