Cryogenic Pressure and Lifetime Studies of a Defect Related Emission in Heavily Silicon Doped GaAs

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We have used cryogenic high pressure measurements and lifetime studies to investigate a defect related emission at 1.269 eV in silicon doped GaAs. The pressure measurements prove that the 1.269 eV photon energy is relative to the conduction band. This implies a deep defect level at 0.30 eV above the valence band and an electron capture process from near the conduction band into the defect. The defect level moves up in the bandgap at a rate of (21 ± 3) meV/GPa. Between 20 K and room temperature the defect emission lifetime remains constant at (0.63 ± 0.25) ms, while the intensity decreases over this same range. We explain this surprising result using an intradefect emission process. These results are consistent with a vacancy related defect level, possibly stemming from a gallium vacancy–silicon at gallium (second-nearest-neighbor) defect complex.

1. Introduction

Defects and defect complexes which occur in heavily doped GaAs (and other semiconductors) have been given much long-term attention due to their technological relevance and the scientific questions they raise. High dopant concentrations (>10^{19} cm^{-3}) produce defects and defect complexes in sufficient quantity to be significant and to be observed. Most research has focused on isolated point defects and on nearest-neighbor point-defect pairs. Much less has been done on defect complexes involving second-nearest-neighbor point-defect pairs. Recently, two specific defect complexes have been discussed, which appear in moderately to heavily silicon doped GaAs [1]. These complexes have been put forth as being partially responsible for the reduction of free-carrier concentrations when doping levels exceed 10^{19} cm^{-3} [2].

In this paper, we summarize photoluminescence (PL) experiments examining defect emission at 1.269 eV. A more complete report has been published in [3, 4]. This emission was observed prior to current crystal growth methods such as molecular beam epitaxy (MBE) [5]. However, neither hydrostatic pressure nor emission lifetime studies have been conducted. Here, we report the results of these studies which provide a more detailed picture of the emission process.

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2. Experimental Details

The silicon doped GaAs was grown by MBE at 580°C on undoped GaAs substrates. Growth layer thicknesses ranged from 2000 to 6000 Å. Carrier concentrations were determined by Hall measurements and confirmed with Raman measurements of the phonon-plasmon energy. For samples exhibiting defect emission, carrier concentrations were very high (2.0 × 10^{16}, 4.9 × 10^{17}, and 8.6 × 10^{18} cm^{-3}). The pressure studies were done with a miniature diamond-encrusted cell immersed in liquid nitrogen. The lifetime studies were all conducted at ambient pressure at temperatures ranging from 20 K to room temperature. More details may be found in [3, 4].

![Graph showing energy levels](image)

Fig. 1. Spectra of silicon doped GaAs (4.9 × 10^{17} cm^{-3}), at three representative temperatures, showing peak A, the defect related emission discussed in this paper. The inset shows the linewidth increase with temperature, which is analyzed within the configuration-coordinate (CC) model. The curve shows the result of the fit.
Photoemission spectra of one sample are shown in Fig. 1 at three temperatures. We focus here on the defect emission (A) near 1.269 eV. Band C is the Barolet-Moss shifted bandgap emission which blueshifts with increasing carrier concentration. We observe no corresponding blueshift in band A, as did Kajikawa (6) in Se doped GaAs. This implies an interesting difference between the emission processes in GaAs:Si and GaAs:Se. Fig. 2 summarizes the effect pressure has on the peak energy of band A. The crossover behavior near 3.9 GPa proves that the emission process stems from an upper level near the band edge to the defect level 300 meV above the valence band. The line shape is Gaussian and its width remained constant below crossover, showing less than a 10% reduction above crossover. The emission process is depicted in the inset to Fig. 2. Using the defect emission pressure shift and that of the bandgap (both below and above crossover) [7], the deep level shifts at a rate of (23 ± 1) meV/GPa. From the method developed by Samara et al. [8], we determine a volume deformation associated with the radiative process to be (1.7 ± 0.6) Å³.

**Fig. 2.** Peak emission energy (from Gaussian fits to spectra) vs. pressure. The two distinct steps occur near 3.3 GPa indicating that the emission is from conduction band into a deep defect level, as shown in the inset.
4. Lifetime Measurements

Two lifetimes were obtained for the measured decay: \( n = 5.0 \) and \( n = 6.0 \) ns (20 E). The short lifetime component stems from the tail of band C. The longer lifetime component is assigned to the defect related emission. Therefore, we focus our attention on this lifetime.

Data obtained were temperature independent with an average value of \( (0.63 \pm 0.05) \) ns over the 30 to 200 K range. Above 200 K, extremely weak intensities prevented accurate determination of the decay curves. The temperature independence is surprising, since the defect emission continuous-wave (CW) intensity is observed to decrease above 100 K by a factor of \( n \). Typically, a decrease in intensity is due to the increasing presence of nonradiative decay paths, which also influences the observed lifetime. (The bandgap emission lifetime decreased from 0.65 to 0.46 ns over this temperature range.) The intensity falloff implies an activation energy of \( (1.9 \pm 0.2) \) meV for both 4.9 \( \times 10^{17} \) and 8.6 \( \times 10^{16} \) cm\(^{-3}\) samples. Thus, activation is not associated with the position of the Fermi level. What is needed now are equilibrium measurements (PL excitation) to better understand the location of the excited states and compare them with the interpretation below.

5. Discussion and Conclusions

Evidently, the observed decrease in the CW intensity of the defect emission over this temperature range stems from a decrease in the number of available electron-hole pairs. This decrease is interpreted as being due to thermal activation of electrons from the upper level (into the conduction band states) competing with the thermalization of carriers. The decrease in CW intensity is a result of the thermal activation of electrons from a level which is discrete and lies \( \approx \Delta E \) below the conduction band states. Alternatively, \( \Delta E \) may be the signature of a metastable state, but we have no supporting evidence for this assertion. Line width analyses within the configuration-coordinate (CC) model [9 to 11] are consistent with a vibrational interaction energy of \( (44 \pm 5) \) meV = \( (350 \pm 40) \) cm\(^{-1}\) which agrees with a silicon vibration causing the loss.

Results are shown in the inset to Fig. 1, and were consistent for the 4.9 \( \times 10^{17} \) and 8.6 \( \times 10^{16} \) cm\(^{-3}\) samples. The two processes, i.e., thermalization and reactivation of electrons, are very fast (\( \approx 10^{8} \) sec) and take place on the same time scale, effectively reducing the number of electrons trapped in the upper level of the defect complex. The defect recombination, which is much slower than these two processes, still takes place in the same manner as at lower temperatures without any competing processes on its time scale. The excess holes trapped on the vacancies may subsequently recombine with excess conduction band electrons via nonradiative transitions which are shown than the defect recombination. Since these transitions are slower, they do not affect the lifetime of the defect recombination.

The entire photoluminescence picture proposed here is as follows. Holes are first produced in the defect complex by one of two processes. Incident photons are absorbed by promoting electrons out of the defect complex ground state (process A in Fig. 3) or out of the valence band (not shown). In the latter, holes can thermalize into the defect level. In either case the defect complex becomes positively charged. Second, process B shows the defect complex capturing an electron, either spontaneously from the ample number of electrons present in the conduction band due to doping. This leaves the defect neutral,
but in its first excited state, which is a silicon donor-like level. The step observed (represented by C) is the radiative transition of the excited electron back into the ground state. Finally, the defect complex relaxes causing a volume deformation. This type of “self-activated” luminescence has been reviewed by Shirono [11] for defects in ZnS and later extended to defects in III–V compounds (e.g., see [5]). The purpose of this diagram is to relate the energy scales of the defect levels with the conduction and valence states, which is primarily established by the high pressure results.

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