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CORRELATION OF COMPENSATION IN Si-DOPED GaAs BETWEEN ELECTRICAL AND OPTICAL METHODS

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The compensation in Si-doped GaAs by metal organic vapor phase epitaxy was studied as a function of electron concentration and growth temperature by means of photoluminescence and Hall effect measurements. The PL spectra show peaks due to Si donor–Si acceptors (Si_{Ga}–Si_{As}) and Si-related complex-defects transitions, which may be attributed to Si donor coupled to a group III elemental vacancy (Si_{Ga}–V_{Ga}) complexes. We showed the importance of each of these defects pair to the optical properties, as it is strongly dependent on the growth parameters. The defects pair are responsible for autocompensation and confirmed by electrical measurements. © 1998 Elsevier Science Ltd. All rights reserved

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1. INTRODUCTION

It is now well established that the Si-doped GaAs epitaxial layers are routinely employed at moderate to heavy doping levels in many devices of interest. For example, in p^+–n GaAs solar cells they form the base and buffer layers of n^+-GaAs of 1×10^{18} cm^{-3} can be used to provide back-surface reflection of minority-carriers and an increase in the photovoltaic conversion efficiency. In high performance submicrometer GaAs-MESFETs, highly doped ($\sim 1 \times 10^{18}$ cm^{-3}) channel layers have been employed [1]. Being a group IV element, it exhibits self-compensation to a much smaller extent. It is well accepted that at low Si concentrations, the Si atoms enter into the lattice mainly as a simple substitutional impurity at the group III element sites (Ga), acting as a donor (Si_{Ga}) and at the As sites, acting as an acceptor (Si_{As}) [2–5]. The latter becoming increasingly important as the Si concentration increases, causing a saturation of the free electron concentration. Heavily doped films present a strong compensation of the free electron concentration. This compensation has been attributed in GaAs mainly to a complex defect formed by a donor atom coupled to a group III element vacancy (Si_{Ga}–V_{Ga}), the so-called self-activating center [6]. This complex defect give rise to a broad photoluminescence line centered about 1.2 eV for GaAs [7] and 1.35 eV for $Al_{0.3}Ga_{0.7}As$ [6] samples. Another deep photoluminescence feature about 1.05–1.28 eV has been attributed to a Si_{Ga}–Si_{As} pair defect [8, 9] and responsible for the compensation. Maguire *et al*. [10] investigated Si doped GaAs by using local vibration modes (LVM), Hall effect and secondary ion mass spectroscopy (SIMS) and concluded that the [Si–X] was tentatively attributed to the well-known self-activated center (Si_{Ga}–V_{Ga}). The LVM results do not necessarily exhaust the possibilities of forms of Si incorporation. Souza and Rao [8] mentioned that in GaAs, the Si incorporation is extremely complex and highly dependent on growth conditions. Photoluminescence and electrical experimental studies, such as Hall effect measurements were used to understand the dopant behavior at high doping concentrations and growth temperatures. In this communication, we show some evidence of the presence of Si_{Ga}–Si_{As} pair defects by studying Si doped GaAs grown under different silane (SiH_4) partial pressures and different growth temperatures. These Si_{Ga}–Si_{As} defect pairs are responsible for reducing free-carrier concentration of higher Si doping levels due to compensation effects.

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2. EXPERIMENTAL DETAILS

The Si-doped GaAs epitaxial layers were grown by metal organic vapor phase epitaxy (MOVPE) on semi-insulating GaAs (1 0 0) substrates with an offset by 2° towards [1 1 0] direction. The source materials were trimethylgallium (TMGa), arsine (AsH_3), (104 ppm) silane (SiH_4) as an *n*-type dopant and palladium purified H_2 as a carrier gas. During the growth, the pressure inside was kept at 100 Torr and the growth temperature was varied from 600°C to 725°C. TMGa and AsH_3 flow rate was varied from 10 to 20 SCCM and 30 to 50 SCCM, respectively. The total flow rate was about 2 SLPM. The doping concentrations were determined by using Hall measurement. Hall effect measurements (Van der Pauw method) were carried out at 300 K to determine the mobility (Hall factor $r_H = 1$). *N*-type layers with thicknesses of about 2 μm were chosen for analysis to reduce thickness measurement errors. Electron densities in the range of 1×10^{17}–1.5×10^{18} cm^{-3} were measured. Low temperature (4.2 K) photoluminescence (LTPL) measurements using 5145 Å excitation from an argon ion laser and 100 mW laser power were carried out.

3. RESULTS AND DISCUSSION

Figure 1 shows the electron concentration as a function of SiH_4 partial pressure. The electron concentration increases monotonically with SiH_4 mole fraction, which is consistent to that reported by Bass [11] and compensates at the concentration of 1.5×10^{18} cm^{-3}. In MOVPE growth, Si, the amphoteric dopant is found to incorporate preferentially on one sublattice over a fairly wide range of dopant concentrations. At higher dopant concentrations, population of the other sublattices can become energetically more favourable resulting in both donor and acceptor formation. This autocompensation limits the maximum carrier concentration that can be achieved in the semiconductor with an amphoteric dopant. The incorporation of an amphoteric dopant on a particular site is considered to result from the combination of thermodynamic, electronic and chemical effects [12]. The electron concentration increases with increasing SiH_4 partial pressure up to 2.9×10^{-5} Torr and then decreases, due to autocompensation. As the SiH_4 partial pressure increases further, the inactivated concentration increased relatively with the doped concentration, indicating the limits of free carrier concentration. The decrease of free-carrier concentration in heavily doped *n*-type GaAs is a well-known phenomenon based upon two main models. One involves amphoteric native defects with strong Fermi level dependent defect formation energy [13, 14] and the other involves electronic occupation of a highly localized state of the donor-related DX center [15]. There are at least other two possible mechanisms responsible for the reduction in the number of electrons: (1) inactivation of the Si donors, i.e. complex formation and (2) charge compensation, i.e. generation of remote acceptors. Subsequently, the actual quantification of Si-atomic concentration would confirm the possible mechanisms and these studies are in progress in terms of secondary ion mass spectroscopy (SIMS). In the recent study of Si doped GaAs by Fushimi *et al.* [16], they pointed out that the limit of free-carrier concentration in the heavily doped layers is caused by gallium vacancy (V_{Ga}) and not by electron occupation of a highly localized state of the donor-related DX center. This autocompensation can be confirmed by taking the optical properties of the films using LTPL spectroscopy.

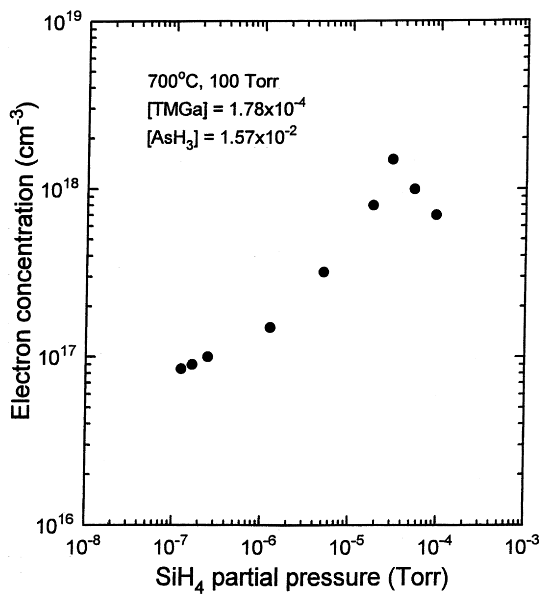

Fig. 1. Electron concentration of Si-doped GaAs as a function of SiH_4 partial pressure.

Figure 2 shows the photoluminescence spectra at 4.2 K in the concentration range of 1×10^{17}–1.5×10^{18} cm^{-3} for the samples studied in Fig. 1. The spectra were measured with LN_2 cooled Ge photodetector whose operating range is about 0.7–1.9 eV, while resolution was kept at about 0.5 meV. The excitonic PL main peak energy shifted to higher energy as the electron concentration increased, which is primarily due to Burstein–Moss effect [17]. According to Burstein and Moss [17], this shift results from the filling of the conduction band. From Fig. 2, it is seen that the sample is autocompensated, when the electron concentration greater than 1.5×10^{18} cm^{-3} in our present growth conditions. The PL spectra corresponding to the electron concentrations 1×10^{18} cm^{-3} and 7×10^{17} cm^{-3} are plotted as inset in Fig. 2. In addition to the near band peak, one observes a broad band with different peaks at around 1.05 and 1.2558 eV. The presence of these peaks

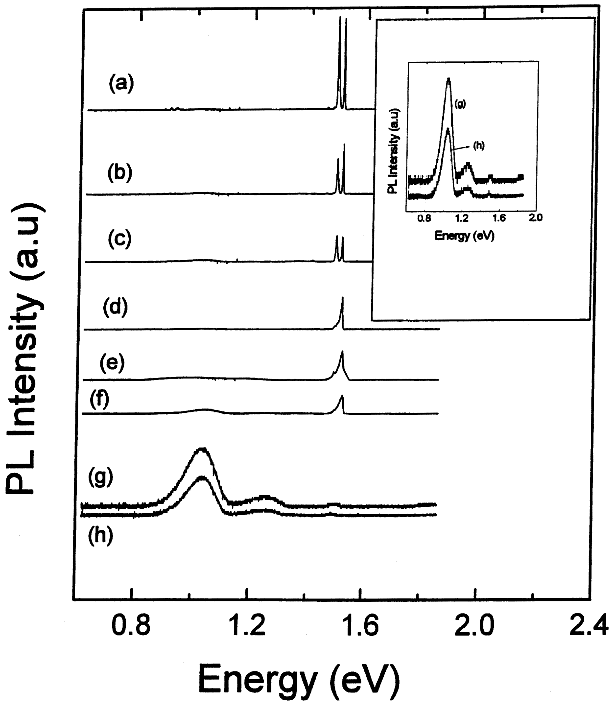

Fig. 2. 4.2 K PL spectra of Si-doped GaAs epilayers for various electron concentrations. The electron concentrations are (a) 1×10^{17} cm^{-3}, (b) 1.5×10^{17} cm^{-3}, (c) 3.2×10^{17} cm^{-3}, (d) 8×10^{17} cm^{-3}, (e) 9×10^{17} cm^{-3}, (f) 1.5×10^{18} cm^{-3}, (g) 1×10^{18} cm^{-3} and (h) 7×10^{17} cm^{-3}.The inset shows the electron concentrations due to (g) 1×10^{18} cm^{-3} and (h) 7×10^{17} cm^{-3}, respectively. The growth parameters are: Substrate temperature = 700°C, [TMGa] = 1.78×10^{-4} and [AsH_3] = 1.57×10^{-2} and SiH_4 partial pressure ranging from 1.24×10^{-7} to 9×10^{-5} Torr.

leads one to believe that possibly this PL band involves more than one emission. In these PL spectra, one can find that, as Si partial pressure increases the lower energy emissions are more favoured. These deep photoluminescence feature about 1.05–1.28 eV has been attributed to a Si_{Ga}–Si_{As} pair defects [8, 9]. The 1.20 eV PL emission in GaAs has been extensively studied and is attributed to the complex (Si_{Ga}–V_{Ga}) [18]. A peak at around 1.4894 eV was observed at higher doping level, most clearly seen at the SiH_4 partial pressure greater than 2.9×10^{-5} Torr of inset Fig. 2. The peak is probably associated with the shallow acceptor, Si_{As} [18]. The broad, lower energy emission with a peak energy of ≈1.05 eV (inset Fig. 2) is accompanied with the Si_{Ga}–V_{Ga} complex for the highest SiH_4 partial pressure. During the process of identifying of this characteristics emission it should be kept in mind that the Si concentration is high and that even Si precipitates have been formed [19]. Therefore, Si_{Ga} atoms remain present in the solid and their concentration may even have increased at this higher SiH_4 concentrations. Gallium vacancies, however, could have been occupied by additional Si atoms. Hence, the simplest mode of understanding is to replace the gallium vacancy in the Si_{Ga}–V_{Ga} complex by a species which is likely to be enhanced at high SiH_4 concentrations. The most likely candidate is Si_{As}, since the compensated character of the samples implies that also the Si_{As} concentration increases as a function of SiH_4 partial pressure. The characteristics emission at 1.05 eV therefore may tentatively be attributed to the Si_{Ga}–Si_{As} [9] complex. One can propose that Si atoms may be incorporated on both Ga (Si_{Ga}) and As (Si_{As}) lattice sites and that, the proportional Si atoms occupying the latter sites increases at higher total Si concentration. Si_{As} centers are acceptors and so the expected free carrier concentration would be given by $n = [Si_{Ga}]-[Si_{As}]$. From this figure, it can also be seen that there is no peak around 1.05–1.28 eV on those samples grown below SiH_4 partial pressure of 2.9×10^{-5} Torr. Therefore, the peaks around 1.05–1.28 eV were present in those samples grown only at the SiH_4 partial pressures greater than 2.9×10^{-5} Torr and indicates that the film is compensated. It is a direct observation of autocompensation, by photoluminescence spectroscopy and confirmed by electrical methods and *vice versa*.

Figure 3 shows the electron concentration and Hall mobility as a function of growth temperatures for a given

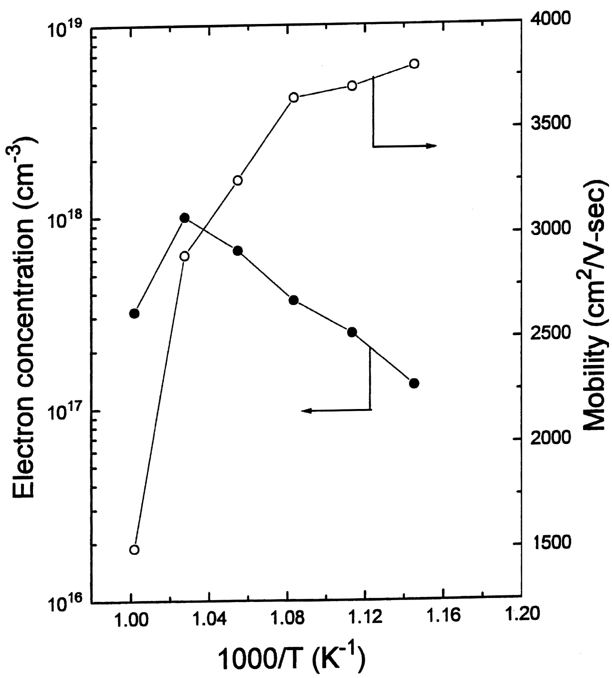

Fig. 3. 300 K electron concentrations and electron mobilities for Si-doped GaAs epilayers grown under various growth temperatures. The growth parameters are: [SiH_4] = 5.18×10^{-7}, [TMGa] = 1.78×10^{-4} and [AsH_3] = 1.57×10^{-2}.

TMGa, SiH_4 and AsH_3 mole fractions. The electron concentration is observed to increase as the growth temperature increases for a fixed SiH_4 mole fraction and is believe to be a result of increasing decomposition rate of SiH_4 with increasing temperature. The electron concentration is equivalent to the Si concentration in most cases ($n \approx [Si]_{GaAs}$). The electron mobility exhibited a decrease with increasing growth temperature. From this figure, it is also seen that the electron concentration decreases with increasing growth temperature above 700°C, due to autocompensation and is further confirmed by Hall mobility data. This autocompensation, can further be confirmed by LTPL spectroscopy of the effect of growth temperature on the photoluminescence spectra.

Figure 4 shows the photoluminescence spectra at 4.2 K for all the samples studied in Fig. 3. The excitonic PL main peak energy shifted to higher energy as the electron concentration increased, which is primarily due to Burstein–Moss effect. From the Fig. 3 it is seen that the sample is autocompensated when the growth temperature is greater than 700°C in our present growth conditions. The PL spectrum corresponding to the growth temperature 725°C is plotted inset in Fig. 4. The PL spectra shows a strong dependence on growth temperature. From this figure, it can also be seen that there is no peak around 1.05–1.28 eV on those samples grown below 700°C, whereas the peak around 1.05–1.28 eV was present in the sample grown at 725°C (inset in Fig. 4). This observation confirms that the film is autocompensated grown above 700°C and exhibits consistently between the photoluminescence and electrical methods as well.

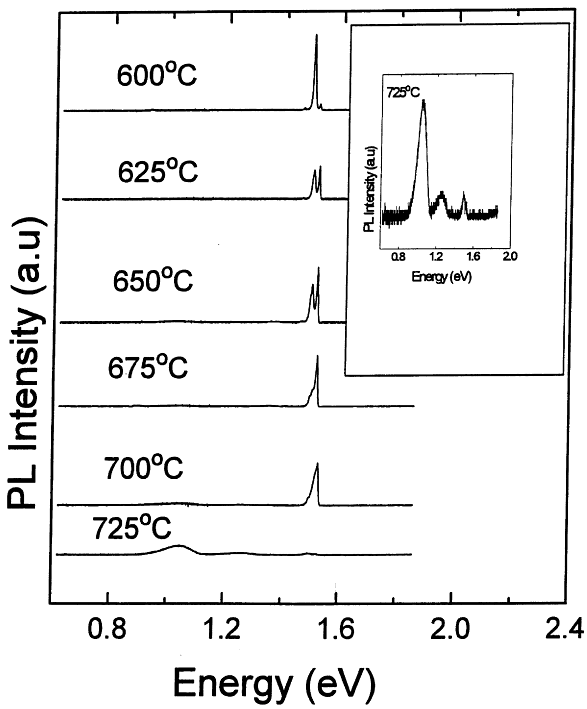

Fig. 4. 4.2 K PL spectra of Si-doped GaAs epilayers for various growth temperatures. The growth parameters are: $[SiH_4] = 5.18 \times 10^{-7}$, $[TMGa] = 1.78 \times 10^{-4}$ and $[AsH_3] = 1.57 \times 10^{-2}$. The inset shows the PL spectrum corresponds to the growth temperature at 725°C.

4. CONCLUSIONS

In conclusion, we have studied the Si doping in GaAs layers grown by MOVPE. Our results indicate the presence of Si complex defects, which are tentatively attributed to Si_{Ga}–Si_{As}. The Si_{Ga}–Si_{As} pair defect is also present in heavily doped samples and also in the samples grown at higher growth temperatures. The photoluminescence spectra shows a strong dependence on electron concentration and growth temperatures. We have demonstrated the direct correlation of compensation in both electrical and optical methods.

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