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Title Photoluminescence of Zn- and Si-doped GaAs epitaxial layers grown by MOCVD

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Photoluminescence of Zn doped and Si doped GaAs epitaxial layers grown by MOCVD

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Low temperature photoluminescence spectroscopy was used to study the band gap shrinkage in Zn and Si doped GaAs films grown by MOCVD technique. The PL experiments were carried out as a function of hole concentration (10^{17}-1.5×10^{20} cm^{-3}) and electron concentration (10^{17}-1.5×10^{18} cm^{-3}). The main peak shifted to lower energy and the full width at half maximum (FWHM) increases with increasing hole concentrations. But in Si doped films the main peak shifted to higher energy and the FWHM increases with increasing electron concentrations. We have obtained an empirical relation for FWHM of PL, $\Delta E(p)$ (eV) $= 1.15 \times 10^{-8} \, p^{1/3}$ and for Si doped films $\Delta E(n)$ (eV) $= 1.4 \times 10^{-8} \, n^{1/3}$. We also obtained an empirical relation for the band gap shrinkage, $\Delta Eg(eV) = -2.75 \times 10^{-8} \, p^{1/3}$ in Zn doped GaAs as a function of hole concentration and ΔEg (eV) $= -1.45 \times 10^{-8} \, n^{1/3}$ in Si doped GaAs as a function of electron concentration. These values indicates a significant band gap shrinkage at high doping levels. These relations are considered to provide a useful tool to determine the hole/electron concentration in Zn/Si doped GaAs by low temperature PL measurement, respectively.

INTRODUCTION

The effect of p-type and n-type heavy doping ($>10^{18}$ cm^{-3}) in GaAs is an important issue of the optical and electrical properties not only from a fundamental understanding but also for the device applications, such as heretojunction bipolar transistors (HBTs),laser diode,contact layer of double heterojunction bipolar transistor (DHBTs), solar cell, metal semiconductor field effect transistors (MESFETs) and high electron mobility transistors (HEMTs). The heavy doping affects the density of states, band structure, carrier mobility, absorption, luminescence properties and hence the device properties. Also the heavy doping changes the band gap narrowing (BGN) or band gap shrinkage due to the formation of density of states, and the tails are resulted from inhomogeneous impurity distribution. Another important phenomenon occurring in the heavily donor-doped semiconductors will be an increase in the inter band transition energy due to the filling of the conduction band by electrons, that is known as the Burstein-Moss effect [1]. In HBTs, the heavy p-type doping effects the shrinkage of band gap of the base, which enhances the emitter injection efficiency, thus affecting the performance of the Np$^+$n (N, n and p$^+$ are electron and hole densities) HBTs. Band gap shrinkage due to heavy doping is a well known phenomenon in III-V compound semiconductors, particularly observed in GaAs by photoluminescence (PL) spectroscopy [2-6]. In the heterojunction-based devices, the band gap shifts due to heavy doping result in valence and conduction band discontinuity of the heterojunction interface.

The p-type doping in GaAs can be obtained either of C, Be, Zn , or Mg as doping sources. Among these doping sources Zn is the most common dopant in GaAs and AlGaAs, although the diffusion coefficient of Zn in these III-V compound semiconductors is high. Still it is preferred because Zn precursors can be handled very easily and high doping efficiency (10^{16}-10^{20} cm^{-3}), uniform doping can be obtained easily. The n-type doping in GaAs can be obtained either of Si, S, Ge, Sn, Se, or Te as doping sources. Among these doping sources Si is commonly used as an intentional n-type dopant in GaAs and related compounds. It has an extremely low diffusivity in GaAs[7], which makes it attractive for device fabrications that involves the high temperature post-growth processing steps. Since the Si has extremely low diffusivity in GaAs and high doping in GaAs by Zn precursor can be obtained very easily, this prompted us to conduct a systematic study of Si doping in GaAs by MOCVD approach.

PL spectroscopy is the most common characterization technique for investigating the distribution of defects, concerning the type and heavy doping effect in GaAs, hence employed in our work. It is a nondestructive and noncontact technique for examining the band structure and luminescence properties of GaAs. The luminescence properties are dependent on the growth conditions (or methods), impurity species, doping concentrations, and growth temperatures. After thorough investigation of Zn/Si doped GaAs, we have suggested a relationship of full width at half maximum (FWHM) versus hole/electron concentration of Zn/Si doped GaAs and band gap shrinkage, which could be considered a useful tool to determine the hole/electron concentration in Zn/Si doped GaAs by low temperature PL measurement.

EXPERIMENTAL

The Zn/Si doped p/n-type GaAs were grown in a low pressure horizontal MOCVD reactor on both Cr doped semi-insulating and Si doped n^+-GaAs (100) substrates with an offset by $2°$ towards [110] direction. The source materials were trimethylgallium (TMGa), (100%) arsine (AsH_3), dimethylzinc (DMZn) as a p-type dopant, (104 ppm) silane (SiH_4) as a n-type dopant and palladium purified H_2 as a carrier gas. During the growth the pressure inside the reactor was kept at 100 Torr and the growth temperature was varied from 550°C to 725°C. TMGa flow and AsH_3 flow rate were 10 SCCM and 50 SCCM, respectively. The total flow rate was about 2 SLPM. The details of the growth procedure can be found elsewhere [8].

The doping concentrations were determined by using both Bio-Rad electrochemical capacitance-voltage (ECV) polaron profiler and Hall measurement. Hole densities in the range of 10^{17} - 1.5×10^{20} cm^{-3} and electron densities in the range of 10^{17} - 1.5×10^{18} cm^{-3} were measured.

PL measurements were carried out using a MIDAC Fourier Transform PL (FTPL) system at a temperature of 4.2K and 100 mW laser power. Argon ion laser operating at a wavelength of 5145A° was used as a source of excitation. The exposed area was about 3mm^2. PL signal was detected by a LN$_2$ cooled Ge-Photodetector whose operating range is about 0.75-1.9 eV, while resolution was kept at about 0.5meV.

RESULTS AND DISCUSSION
PL spectra as a function of hole concentrations

Fig. 1 shows the 4.2K PL spectra of Zn doped GaAs for hole concentrations of (a) 4.5×10^{17} cm^{-3}, (b) 3.8×10^{18} cm^{-3}, (c) 8×10^{18} cm^{-3}, (d) 2.9×10^{19} cm^{-3}, (e) 1.5×10^{20} cm^{-3}, respectively. The FWHM, $\Delta E(p)$ of the (e-A) peak at 4.2K of PL spectra increases with increasing hole concentration. The broadening of FWHM is similar to the C doped GaAs [6], Be doped GaAs [3] and Zn doped GaAs [2] and can be explained by band-to-band optical transitions with and without momentum (K) conservation between the conduction and valence bands [4]. Alternatively, this can be explained as the impurity band merges with the valence band edge and it becomes band tail states at high doping concentrations. Because of this phenomena, the optical transitions between the conduction and valence band are broadened, the FWHM of PL spectra increases. From the data we have obtained an empirical relation for FWHM of Zn doped GaAs,

$$\Delta E(p)\,(eV) = 1.15 \times 10^{-8}\, p^{1/3} \qquad (1)$$

with the concentration range between 1×10^{17} and 1.5×10^{20} cm^{-3}. The results are compared with C-doped GaAs[9] and shown in Fig. 2.

Band gap shrinkage due to Zn doping effect

The main peak energy shifted to lower energy as the hole concentration increased, which is primarily because of doping induced band gap shrinkage or band gap narrowing (BGN). We have determined the band gap, E_g of heavily doped GaAs, by a linear extrapolation to the energy axis, using a function of the type $f(E) = A\,(E-E_g)^{1/2}$, of the spectrum to the background level following the work by Olego and Cardona [4]. This method was used by several authors for determination of E_g.

Fig. 3 shows the band gap shrinkage of Zn doped GaAs in the range 4.5×10^{17} to 1.5×10^{20} cm^{-3}, as a function of hole concentrations. In this figure, we have also plotted the reported results for Zn, Be and C doped GaAs measured at temperatures between 4.2K and 77K, because the band gap shrinkage is independent of temperature [4]. The measured band gap shrinkage of carrier

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concentration of Be, C and Zn doped GaAs, exhibited consistent agreement between each other [3,4,10-12]. In general, the band gap shrinkage is proportional to the hole concentration of the form $p^{1/3}$, thus it can be represented by
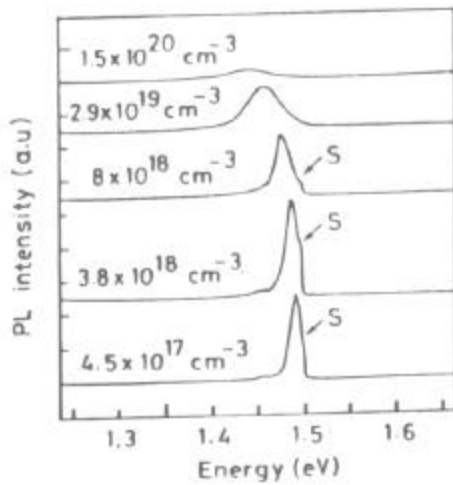

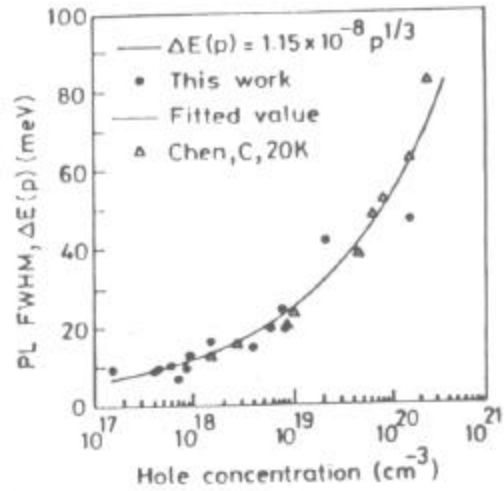FIG. 1. 4.2K PL spectra of Zn-doped GaAs epilayers for various hole concentrations.

FIG. 2. FWHM of 4.2K PL versus hole concentrations.

$$\Delta E_g = E_g \text{(doped)} - E_g \text{(pure)} = - Bp^{1/3} \qquad (2)$$

where B has been adjusted to give the measured value of E_g at higher hole concentration and the minus sign signifies the band gap shrinkage at high concentrations. The empirical relation for band gap narrowing with our datas can be written as

$$\Delta E_g = - 2.75 \times 10^{-8} \, p^{1/3} \qquad (3)$$

where E_g is in eV and p in cm^{-3}.

We have made an attempt to fit our experimental data to the expression suggested by S.C. Jain [13],

$$E_g = E_g (0) - \Delta E_g (p) \qquad (4)$$

Where $\Delta E_g (p) = a \times p^{1/3} + b \times p^{1/4} + c \times p^{1/2}$, a, b and c are the coefficients that represent the effects of the BGN due to majority - majority carrier exchange, minority - majority correlation and carrier - ion interaction respectively. For p-type GaAs, the constants a, b and c are 9.83×10^{-9}, 3.9×10^{-7} and 3.9×10^{-12}, respectively, where p is the hole concentration in cm^{-3} and E_g (p) in eV. The band gap shrinkage result also plotted in Fig. 3 given by Casey and Stern [14].
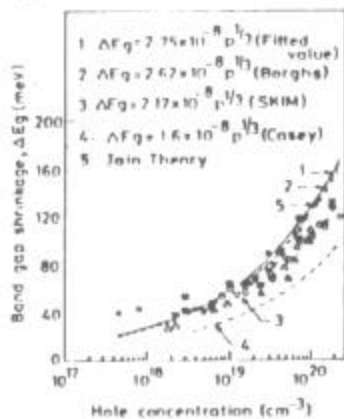

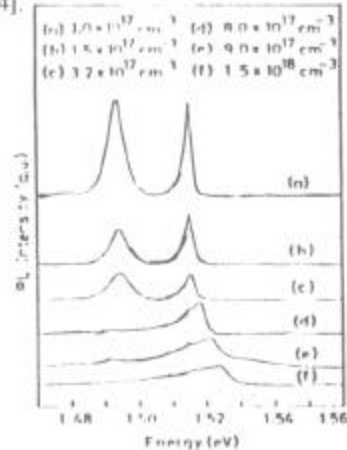FIG. 3. The band gap shrinkage of Zn doped GaAs epilayers for various electron concentrations.

FIG. 4. 4.2K PL spectra of Si doped GaAs epilayers as a function of electron concentration.

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PL spectra as a function of electron concentration

Figure 4 shows the 4.2K PL spectra of Si-doped GaAs for electron concentrations of (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) 1×10^{18} cm^{-3}, respectively. The peak at 1.493 eV has been attributed to band-to-acceptor (B-A) transitions involving residual carbon (C) impurities present in MOVPE GaAs [15]. This B-A transitions are observed at electron concentration 1×10^{17} cm^{-3} and decreases with increasing doping concentration. The similar type of observation was made by Sieg and Ringle [5] in MOVPE grown Si-doped InP by 16K PL measurement. Beyond 3.2×10^{17} cm^{-3} in our case, only one broad emission band is found, and the peak maximum of the dominant emission E_{max} is shifted monotonically towards higher energy with increasing free-carrier concentration. According to Burstein and Moss, this shift results from the filling of conduction band. The asymmetry observed in the spectra of Fig. 4 at $n > 3.2 \times 10^{17}$ cm^{-3} strongly indicates that indirect (without k-selection) B-B or B-A transitions dominate the emission across the optical gap. The contribution of indirect transitions in the luminescence of degenerate n-type semiconductors has recently been reported for n-type InP [5].

The full width at half maximum (FWHM), $\Delta E(n)$ of the B-B peak at 4.2K of PL spectra increases with increasing electron concentration. The $\Delta E(n)$ increases slowly up to $n \approx 2 \times 10^{17}$ cm^{-3} and increases rapidly with increasing electron concentration. From the data we have obtained an empirical relation for FWHM of Si-doped GaAs,

$$\Delta E(n)\,(eV) = 1.4 \times 10^{-8}\, n^{1/3} \tag{5}$$

with the concentration range between 1×10^{17} and 1.5×10^{18} cm^{-3}. The results are compared with previous studies reported in the literature [16] and shown in Figure 5.

Band gap shrinkage due to Si doping effect

The main peak energy shifted to higher energy as the electron concentration increased, which is primarily because of doping induced band gap shrinkage or band gap narrowing (BGN). However, theoretical calculations [17] for n-GaAs indicate that BGN is strongly wave vector dependent for that material, with the largest shifting occurring at zone centre and much smaller shifts occurring near the Fermi energy. The BGN near the Brillouin zone center is extracted from the low-energy side of our PL spectral peaks and compared with a theoretical estimate of BGN at zone center. Figure 6 shows the band gap shrinkage of Si-doped GaAs in the range 1×10^{17} to 1.5×10^{18} cm^{-3}, as a function of electron concentration. The empirical relation for band gap narrowing with our datas can be written as

$$\Delta E_g = -1.45 \times 10^{-8}\, n^{1/3} \tag{6}$$

where ΔE_g is in eV and n in cm^{-3}.
We have made an attempt to fit our experimental data to the expression suggested by S.C. Jain [13],

$$E_g = E_g(0) - \Delta E_g(n) \tag{7}$$

Where $\Delta E_g(n) = a \times n^{1/3} + b \times n^{1/4} + c \times n^{1/2}$, a, b and c are the coefficients that represent the effects of the BGN due to majority - majority carrier exchange, minority - majority correlation and carrier - ion interaction respectively. For n-type GaAs, the constants a, b and c are 16.5×10^{-9}, 2.39×10^{-7} and 91.4×10^{-12}, respectively, where n is the electron concentration in cm^{-3} and $\Delta E_g(n)$ in eV. These relations are considered to provide a useful tool for determination of hole/electron concentration in Zn/Si - doped GaAs by low temperature PL measurement. Good experimental agreement has been obtained for Eq.(7) in the cases of p-GaSb and p-GaAs [2,13]. In the case of n-GaAs, however, the agreement with experimental is far from satisfactory [3,18], with Eq.(7) giving much larger BGN values than have been observed experimentally by PL. A similar discrepancy occurs even in n-InP [5]. Sieg and Ringel had given the three possible explanation in the cases of n-GaAs and n-InP between the theoretical BGN as calculated from Eq.(7) and experimental BGN as obtained by PL. The details of the discussion can be found in this reference [5].

CONCLUSION

Zn/Si-doped GaAs epitaxial layers grown by low pressure metalorganic vapor phase epitaxy in the hole/electron concentration range $(10^{17}-1.5 \times 10^{20}$ cm$^{-3})$ and $(1 \times 10^{17}-1.5 \times 10^{18}$ cm$^{-3})$, respectively have been investigated by photoluminescence as a function of hole/electron concentrations. From the PL spectra we have obtained an empirical relation of FWHM and band gap shrinkage as a function of
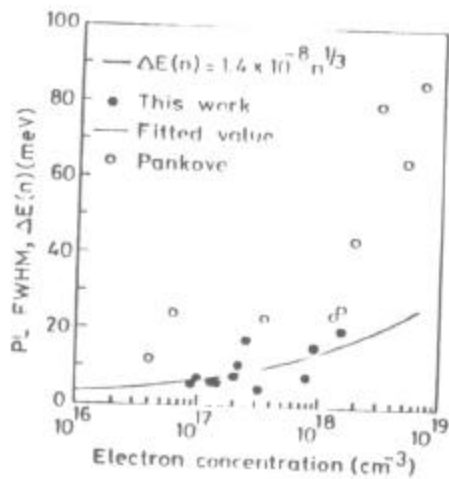
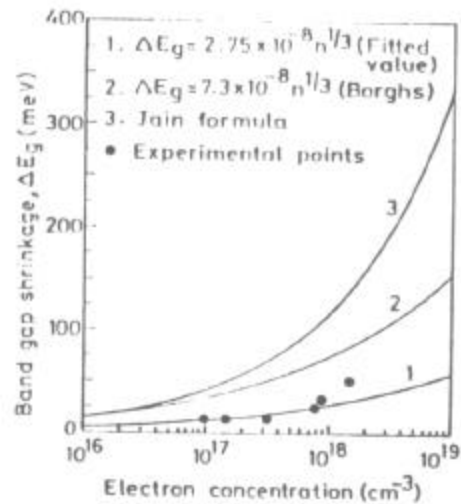**FIG. 5.** FWHM of 4.2K PL versus electron concentrations.

FIG. 6. The band gap shrinkage of Si-doped GaAs epilayers as a function of electron concentration.

hole/electron concentrations. These relations are considered to provide a useful tool for determining the electron concentration by low temperature PL measurement.

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