Zn and Si Incorporation and Band Gap Narrowing in GaAs Grown By LPMOVPE

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Abstract

DMZn and SiH_4 were used as a p and n-type dopants, respectively in GaAs grown by LPMOVPE. The dopant incorporation efficiencies were studied by using the various growth parameters. LTPL was used to study the band gap shrinkage in Zn and Si-doped GaAs films as a function of hole concentration (10^{17}-$1.5x10^{20}$ cm^{-3}) and electron concentration (10^{17}-$1.5x10^{18}$ cm^{-3}). We have obtained an empirical relation for FWHM of PL, $\Delta E(p)$ (eV) = 1.15x10-8 $p^{1/3}$ and band gap shrinkage, ΔEg (eV) = - 2.75x10-8 $p^{1/3}$ in Zn doped GaAs and $\Delta E(n)$ (eV) = 1.4x10-8 $n^{1/3}$, ΔEg (eV) = - $1.45x10^{-8}$ $n^{1/3}$ in Si doped GaAs. These values indicate a significant band gap shrinkage at high doping levels and considered to provide a useful tool to determine the hole/electron concentration in Zn/Si doped GaAs by low temperature PL measurement, respectively.

1. 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. The heavy doping changes the band gap narrowing (BGN) or band gap shrinkage due to the formation of density-of-states. 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]. Band gap shrinkage due to heavy doping is a well known phenomenon in III-V compound semiconductors. 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 [2]. 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 [2]. PL spectroscopy was used to study the heavy doping effect, examining the band structure and luminescence properties of GaAs. 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.

2. 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 by using dimethylzinc (DMZn) as a p-type dopant and (104 ppm) silane (SiH_4) as an n-type dopant, respectively. The details of the growth procedure can be found elsewhere [3,4]. The doping concentrations were determined by using both electrochemical capacitance-voltage (ECV) polaron profiler and Hall measurement. Hole densities in the range of 10^{17} - $1.5 x10^{20}$ cm^{-3} and electron densities in the range of 10^{17} - $1.5 x10^{18}$ cm^{-3} were measured. PL measurements were carried out using a MIDAC Fourier Transform PL (FTPL) system at a temperature of 4.2K, resolution 0.5 meV 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.

3. Results and discussion

3.1. Zn incorporation and band gap shrinkage

The hole/electron concentration increases with increasing DMZn /SiH4 mole fraction. The hole concentration is observed to increase as the growth temperature decreases and the electron concentration increases with increasing growth temperature. The hole concentration increases with increasing AsH_3 and TMGa mole fraction and the growth rate was found to be decrease with increasing AsH_3 and decreasing TMGa mole fraction [5]. The former can be explained by vacancy controlled model. In the TMGa-AsH3 system, the leading reaction to the formation of GaAs can be expressed as:

$$(CH_3)_3Ga + \tfrac{3}{2}H_2 + V_{Ga} \overset{K_1}{\Leftrightarrow} Ga_{Ga} + 3CH_4 \qquad (1)$$

$$\mathrm{AsH_3} + \mathrm{V_{As}} \overset{K_2}{\Leftrightarrow} \mathrm{As_{As}} + \tfrac{3}{2}\mathrm{H_2} \qquad (2)$$

Where K_1 and K_2 are the equilibrium constants of the above reactions, then

$$\frac{[V_{Ga}]}{[V_{As}]} = \frac{K_2}{K_1}\frac{P^3_{CH_4}}{P_{TMGa}}\frac{P_{AsH_3}}{P^3_{H_2}} \qquad (3)$$

An increase in P_{AsH3}/P_{TMGa} will increase in Ga vacancy, hence the incorporation of Zn on the Ga site is increased. The hole concentration is thus increased when the AsH_3 mole fraction is increased. Fig. 1 shows the 4.2K PL spectra of Zn-doped GaAs for hole concentrations of $4.5\mathrm{x}10^{17}$ cm^{-3}, $3.8\mathrm{x}10^{18}$ cm^{-3}, $8\mathrm{x}10^{18}$ cm^{-3}, $2.9\mathrm{x}10^{19}$ cm^{-3}, $1.5\mathrm{x}10^{20}$ cm^{-3}, respectively. The FWHM, $\Delta E(p)$ of the (e-A) peak at 4.2K of PL spectra increases with increasing hole concentration. 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,

$$\Delta E(p)(eV) = 1.15 \times 10^{-8}\, p^{1/3} \qquad (4)$$

with the concentration ranges of 1×10^{17} - 1.5×10^{20} cm^{-3}.

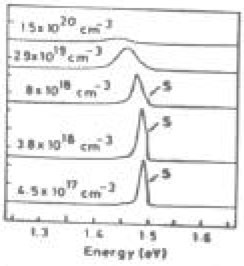

FIG. 1. 4.2K PL spectra of Zn-doped GaAs epilayers.

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 [6].

Fig. 2 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 [6]. The measured band gap shrinkage of carrier concentration of Be, C and Zn-doped GaAs, exhibited consistent agreement between each other [5]. In general, the band gap shrinkage is proportional to the hole concentration of the form $p^{1/3}$, thus it can be represented by

$$\Delta E_g = E_g\,(\mathrm{doped}) - E_g\,(\mathrm{pure}) = -\,Bp^{1/3} \qquad (5)$$

where B has been adjusted to give the measured value of ΔE_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

$$\Delta E_g = -\,2.75 \times 10^{-8}\, p^{1/3} \qquad (6)$$

where ΔE_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 [7],

$$E_g = E_g\,(0) - \Delta E_g\,(p) \qquad (7)$$

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.

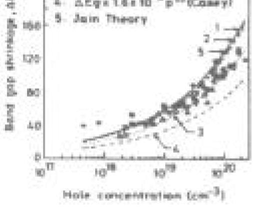

FIG. 2. The band gap shrinkage of Zn-doped GaAs

3.2. Si incorporation and band gap shrinkage

The electron concentration decreases with increasing TMGa flow rates and the growth rates were affected with a linear decrease. This can also be explained by vacancy control model. Since Si as a donor is on the Ga sublattice and under equilibrium its incorporation should be proportional to the concentration of Ga vacancies, V_{Ga} [8]. The doping reaction is:

$$\mathrm{SiH_4} + \mathrm{V_{Ga}} \xrightarrow{K_3} \mathrm{Si_{Ga}} + 2\mathrm{H_2} \qquad (8)$$

From equations (3) and (4) one can write ,

$$\frac{[Si_{Ga}]}{[V_{As}]} = \frac{K_2K_3}{K_1}\frac{P_{SiH_4}}{P_{TMGa}}\frac{P_{AsH_3}}{P^5_{H_2}}P^3_{CH_4} \qquad (9)$$

An increase in P_{AsH_3} will increase in gallium vacancy concentration, hence, the incorporation of Si on Ga site is increased. The electron concentration is thus increased when the AsH_3 mole fraction is increased and hence the PL main peak is shifted towards the higher energy with increasing AsH_3 mole fraction.

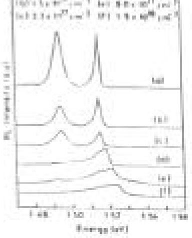

FIG. 3. 4.2K PL spectra of Si-doped GaAs epilayers.

Figure 3 shows the 4.2K PL spectra of Si-doped GaAs for electron concentrations of $1x10^{17}$ cm^{-3}, $1.5x10^{17}$ cm^{-3}, $3.2x10^{17}$ cm^{-3}, $8x10^{17}$ cm^{-3}, $9x10^{17}$ cm^{-3}, $1x10^{18}$ 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 [4]. This B-A transitions are observed at electron concentration $1x10^{17}$ cm^{-3} and decreases with increasing doping concentration. Beyond $3.2x10^{17}$ 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 $n > 3.2x10^{17}$ 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 [9].

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 $n = 2 x 10^{17}$ cm^{-3} and increases rapidly with increasing electron concentration. From the data we have obtained an empirical relation for FWHM of Si-doped GaAs,

$$\Delta E(n) (eV) = 1.4 x 10^{-8} n^{1/3} \qquad (10)$$

with the concentration range of $1x10^{17}$ - $1.5x10^{18}$ cm^{-3}.

Figure 4 shows the band gap shrinkage of Si-doped GaAs in the range $1 x 10^{17}$ to $1.5 x 10^{18}$ cm^{-3}, as a function of electron concentration. The empirical relation for band gap narrowing with our datas can be written as

$$\Delta E_g = - 1.45 x 10^{-8} n^{1/3} \qquad (11)$$

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 [7],

$$\Delta E_g (n) = a x n^{1/3} + b x n^{1/4} + c x n^{1/2} \qquad (12)$$

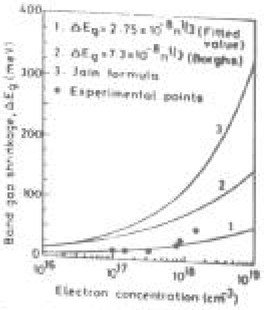

FIG. 4. The band gap shrinkage of Si-doped GaAs

For n-type GaAs, the constants a, b and c are $16.5 x 10^{-9}$, $2.39 x 10^{-7}$ and $91.4 x 10^{-12}$, respectively, where n is the electron concentration in cm^{-3} and ΔE_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.(12) in the cases of p-GaSb and p-GaAs [5,7]. The details of the discussion can be found in this reference [9].

4. Conclusion

Zn/Si-doped GaAs epitaxial layers grown by low pressure metalorganic vapor phase epitaxy in the hole/electron concentration range (10^{17}-$1.5x10^{20}$ cm^{-3}) and ($1x10^{17}$-$1.5x10^{18}cm^{-3}$), 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 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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