Low temperature photoluminescence properties of Zn-doped GaAs

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Abstract

Dimethylzinc (DMZn) was used as a p-type dopant in GaAs grown by low pressure metalorganic chemical vapor deposition (MOCVD). The influence of growth parameters, such as, DMZn mole fractions, growth temperature, trimethylgallium (TMGa) mole fractions, substrate surfaces on the Zn incorporation have been studied. The surface morphology of the layers was measured by scanning electron microscopy (SEM). The hole concentrations and zinc (Zn) incorporation efficiency are studied by using Hall effect, electrochemical capacitance voltage (ECV) profiler, and low temperature photoluminescence (LTPL) spectroscopy as functions of hole concentration \(10^{17} - 1.5 \times 10^{20} \, \text{cm}^{-3}\) and experimental temperatures (4.2–300 K). The hole concentration increases with increasing DMZn and TMGa mole fractions and decreases linearly with increasing growth temperature. The main PL peak shifted to lower energy and the full width at half maximum (FWHM) increased with increasing hole concentration. An empirical relation for FWHM, \(\Delta E_p\), band gap, \(E_g\), and band gap shrinkage, \(\Delta E_g\) in Zn doped GaAs as a function of hole concentration were obtained. These relations are considered a useful tool to determine the hole concentration in Zn doped GaAs by low temperature PL measurement. The hole concentration increases with increasing TMGa mole fraction and the main peak is shifted to lower energy side. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Undoped and Zn-doped GaAs epitaxial layers grown by low pressure metalorganic chemical vapor deposition (MOCVD) [1] are widely used in optoelectronic device fabrications [2]. In addition to high optical and electrical quality of the films, the heavily doped epitaxial film for optoelectronic device applications require mirror smooth surface morphology. The mirror smooth surface morphology and specific concentration of impurity in GaAs by MOCVD can be obtained by controlling the growth temperature. Hence, it is essential to understand the influence of the growth parameters, which control the layer quality.

The effect of p-type heavy doping \( (> 10^{19} \, \text{cm}^{-3}) \) in GaAs is an important issue of the optical and electrical properties not only in the view of a fundamental understanding but also for the device applications. The heavy doping affects the density of states, carrier mobility, absorption, band structures, luminescence properties, and hence the device performance [3,4]. Also, the high doping affects the band gap shrinkage and by a band tail extending into the gap. In the heterojunction-based devices, the band gap shifts due to heavy doping result in valence and conduction band discontinuity of the heterojunction interface [5].

The p-type doping in GaAs can be obtained either of C, Be, Zn, or Mg as 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 [6], and it is preferred because Zn precursors can be handled very easily and high doping efficiency \(10^{16} - 10^{20} \, \text{cm}^{-3}\), uniform doping can be obtained. Zn doping is always exhibiting low memory effects, a relatively small amount of deep level traps [7] and good surface morphology even at high doping levels. S. Z. Sun et al [8] found that the surface morphology of Zn-doped GaAs was more dependent on growth rate than growth temperature when the mole fraction of diethylzinc (DEZn) was \(9.16 \times 10^{-5}\). Because of the different electrical and optical properties of...
Zn doped GaAs from C-doped GaAs [9–13] grown by MOCVD, these properties have been studied extensively by several authors in recent years [14–19]. This prompted us to conduct a systematic study of Zn doping in GaAs by low temperature photoluminescence (PL) measurement.

Low temperature photoluminescence (LTPL) spectroscopy is a common characterization technique for investigating the band structures of GaAs at high doping levels. Band gap shrinkage due to heavy doping is a well known phenomenon in III–V compound semiconductors, particularly observed in GaAs by PL spectroscopy [9,10,20–26]. The luminescence properties are dependent on the growth conditions (methods), doping concentrations, impurity species, growth temperatures, etc. In this paper we are reporting the results from the low temperature luminescence properties of Zn-doped GaAs by PL measurement by varying the hole concentrations, trimethylgallium (TMGa) mole fractions and PL measurement temperatures. After thorough investigation of Zn-doped GaAs, we have suggested a relationship for full width at half maximum (FWHM), band gap and band gap shrinkage of Zn-doped GaAs, which could be considered a useful tool for determining the hole concentration in Zn-doped GaAs by low temperature PL measurement.

2. Experimental

The Zn-doped p-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), arsine (AsH₃), dimethylzinc (DMZn) as a p-type dopant and palladium purified H₂ 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 to 725°C. AsH₃ flow rate was kept constant at 50 standard cm³ min⁻¹ (SCCM) and the TMGa flow rate was varied from 10 to 20 SCCM in order to obtain different growth rates and same stoichiometry. The total flow rate was about 2 standard liter min⁻¹ (SLPM). The growth rate was varied between 470 and 800 Å min⁻¹. The details of the growth procedure can be found elsewhere [27].

The surface morphology of GaAs epilayers was seen under scanning electron microscopy (SEM). The doping concentrations were determined by using both Bio-Rad electrochemical capacitance-voltage (ECV) polaron profiler and Hall measurement. Hall effect by Van der Pauw method was carried out at temperature 300 K for mobility measurement, considering the Hall factor \( r_H = 1 \). The hole concentration does not change appreciably within the temperature range of 77–300 K. The hole concentration measured at 300 K was used in 4.2 and 120 K photoluminescence studies and the same procedure was followed by several authors [14,18,25,28]. P-type layers with thickness of about 1.2 µm were chosen for analysis to reduce thickness measurement errors. Hole densities in the range of \( 10^{17} - 1.5 \times 10^{20} \text{ cm}^{-3} \) were measured.

PL measurements were carried out using a MIDAC Fourier Transform PL (FTPL) system at temperatures ranging from 4.2 to 300 K and 100 mW laser power. Argon ion laser operating at a wavelength of 5145 Å was used as a source of excitation. The exposed area was about 3 mm². PL signal was detected by a LN₂ cooled Ge Photodetector whose operating range is about 0.75–1.9 eV, while resolution was kept at 0.5 meV.

3. Results and discussion

Zn was used as a p-type dopant for GaAs and it is the most common MOCVD p-type dopant for GaAs and AlGaAs. All the Zn-doped GaAs epitaxial layers were grown for this study at a V/III ratio of 87 [29].

3.1. Electrical properties

3.1.1. Effect of variation of DMZn mole fraction and growth temperature

The surface of epilayer is influenced by the growth parameters, such as, pressure inside the reactor tube, growth temperature, substrate orientation, AsH₃/ TMGa mole ratio, etc. The surface of Zn-doped p-type GaAs appears to be mirror smooth over a wide range
of temperatures (600–725°C) in this study. Fig. 1 shows the hole concentration as a function of DMZn mole fraction.

The hole concentration increases linearly with DMZn mole fraction, which is consistent to that described by Glew [30]. The hole concentration was observed to increase as the growth temperature decreases as shown in Fig. 2 for a fixed DMZn mole fraction. The strong temperature dependence of Zn incorporation was believed to be a result of evaporation of Zn atoms from the growth surface due to increased vapor pressure at higher temperatures. Between 600 and 725°C the incorporation activation energy of DMZn from the slope of the Arrhenius plot is around 3.2 eV, which is in agreement with the earlier reported results by Bass and Oliver [31] and Glew [30]. The surface morphology of Zn-doped layers was found polycrystalline in the range of temperature 550 to 575°C and can be seen from the Fig. 3. From this figure we observed that the surface morphology of Zn-doped GaAs not only depend on growth temperature but also on the type of substrate surfaces (semi-insulating or n+ GaAs substrate) of the same growth run. TMGa decomposes rapidly above 500°C in an MOCVD reactor. Between 500 and 550°C cracked AsH3 concentration is normally low. This has been suggested due to the lack of cracked AsH3 concentration on the growth surface [2]. Above 575°C, the concentration of arsenic is significant [2] and plays a major role in the growth kinetics. Hole concentrations of Zn doped GaAs films are known to depend upon AsH3 partial pressures. Therefore, Zn incorporation changes with temperature and decomposed AsH3 concentration. Above 600°C, AsH3 was fully decomposed and Zn incorporation was temperature dependent. For a given TMGa, DMZn, and AsH3 mole fraction, the hole concentration and Hall mobility are also seen in Fig. 2. The hole mobility exhibited a decrease with decreasing growth temperature. This phenomena can be interpreted in terms of pronounced Zn evaporation from the surface of epilayers at higher growth temperature. Another mechanism that may explain these results is temperature dependence of gallium vacancies. Chang et al [16] and Glew [30] observed similar behavior of Zn doped GaAs by low pressure MOCVD reactor using DEZ, and both DMZn and DEZ, respectively.

A vacancy-controlled model may be considered to explain such behavior. In the TMGa-AsH3 system, the leading reaction to the formation of GaAs can be expressed as:

\[ (\text{CH}_3)_3 \text{Ga} + 3/2 \text{H}_2 + V_{\text{Ga}} \rightarrow \text{Ga}\text{As} + 3 \text{CH}_4 \]  

where \( V_{\text{Ga}} \) and \( V_{\text{As}} \) represent the gallium and arsenic vacancies, respectively. Ga\text{As} represents the gallium occupying on gallium site. As Ga is the arsenic occupying on Ga site. Here As must obtain enough energy to overcome the energy barrier. When the growth temperature decreases, the above reaction occurs towards the left and more gallium vacancies tend to appear. Since the incorporation of Zn is proportional to Ga vacancy, the Zn concentration on Ga sites increases at lower growth temperatures.

3.1.2. Effect of growth temperature on growth rate

The change in growth rate as a function of growth temperature for Zn doped GaAs as shown in Fig. 4. It can be seen from this figure that the growth rate increases with increasing growth temperature up to 625°C. But different authors observed [30] different
behavior of growth rate in the temperature range 550–750°C. At high substrate temperatures, the growth rate decreases because of arsenic desorption effects from the growth surface. Between the temperatures 625 and 725°C the growth rate was found to be temperature independent which is similar to that described by Glew [30]. In this temperature region, TMGa is fully decomposed and hence growth rate becomes independent of temperature. In a classic paper, Shaw [35] showed that an examination of growth rate versus temperature allows a general categorization of the process, limiting the growth rate as either mass transport, surface kinetics or thermodynamics. For an exothermic process, such as MOCVD, increasing temperature results in a decrease in the thermodynamically limited growth rate. If the reaction-rate-limits the growth rate, which is termed the kinetically limited case, the growth rate increases with increasing temperature. Since diffusion is a nearly temperature independent process, the growth rate is nearly independent of substrate temperature in the mass-transport-limited case, as also observed by Shaw [35]. The growth rate is nearly independent of temperature of MOCVD growth process in the temperature range from 550 to 750°C, at normal operating pressure. This is indicative of mass-transport-limited growth. At lower temperatures, the growth rate decreases with decreasing temperature which happens to be characteristic of a process-limited by reaction kinetics. The growth rate is proportional to the flux of atoms being transported, usually by diffusion, through the gas phase to the interface, which is identical to the flux of atoms crossing the interface into the solid. Using ordinary growth conditions, keeping temperature between $\approx 550$ and $800°C$, the growth rate is nearly independent of temperature in the mass-transport-limited growth. For surface-kinetically-limited process, the growth rate increases exponentially with increasing temperature. This occurs for the MOCVD growth of GaAs only at temperature below $\approx 550°C$. Since the MOCVD growth process is in the mass-transport limited regime, the growth rate is linearly dependent on the group III partial pressures not the group V partial pressure, which controls the stoichiometry of the semiconductor. This is important because the stoichiometry affects the
dopant and impurity incorporation as well as the concentrations of native defects, i.e. those involving interstitial atoms and vacancies. It is observed that higher the substrate temperature ($T_{\text{sub}}$), higher the available gallium concentration and hence higher growth rates.

3.2. Optical properties

3.2.1. PL spectra as a function of hole concentrations

Fig. 5 (a), (b), and (c) shows the 4.2, 120, and 300 K PL spectra of Zn-doped GaAs for hole concentrations of (a) $4.5 \times 10^{17}$ cm$^{-3}$, (b) $3.8 \times 10^{18}$ cm$^{-3}$, (c) $8 \times 10^{18}$ cm$^{-3}$, (d) $2.9 \times 10^{19}$ cm$^{-3}$, and (e) $1.5 \times 10^{20}$ cm$^{-3}$, respectively. The curves were intentionally offset along the y-axis with respect to each other for better clarity. The same procedure was used for all the other PL spectra in this paper. The FWHM, $\Delta E(p)$, of the donor-to-acceptor (e-A) peak between the temperature 4.2 and 300 K of PL spectra increases with increasing hole concentration. The broadening of FWHM is similar to the C-doped GaAs [28], Be-doped GaAs [24] and Zn-doped GaAs [9] and can be explained by band-to-band optical transitions with and without momentum (K) conservation between the conduction and valence bands [9]. 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 bands are broadened, the FWHM of PL spectra increases. The $\Delta E(p)$ increases slowly up to $p \approx 1 \times 10^{18}$ cm$^{-3}$ and increases rapidly with increasing hole concentration. From the data we have obtained an empirical relation for FWHM of Zn doped GaAs at 4.2 K,

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

with the concentration range between $1 \times 10^{17}$ and $1.5 \times 10^{20}$ cm$^{-3}$. The results are compared with C-doped GaAs [10] and shown in Fig. 6. The value of FWHM is about 10 meV for $p = 1 \times 10^{18}$ cm$^{-3}$, and it increases rapidly at $p > 3 \times 10^{18}$ cm$^{-3}$ due to the appearance of the extra peak which is clearly observed at 4.2 K PL measurement temperature. When the concentration reaches $1.5 \times 10^{20}$ cm$^{-3}$, the value of FWHM is 50 meV.

3.2.2. Band gap shrinkage due to 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). Fig. 7 shows the main PL peak energy, $E_g$, with the hole concentration in the range of $1 \times 10^{17}$–$1.5 \times 10^{20}$ cm$^{-3}$. The $E_g$-$p$ relation is very important for the determination of hole density in the base of heterojunction bipolar transistors (HBTs) and active layer of the laser diodes. The empirical relation for $E_g$-$p$ at 4.2 K by PL measurement can be represented by

$$E_g = 1.52 - 4.1 \times 10^{-6} \times p^{0.215}$$

We have also included the peak energy measured at 120 and 300 K by PL measurement. From this graph, it is seen that the peak energy measured at 4.2 and 120 K are the same and hence the $E_g$-$p$ relation can be used to considered a useful tool for determination of hole concentration at any temperature within 4.2 and 120 K. If this is the case, one should expect the same band gap narrowing (BGN) due to heavy doping in GaAs by low temperature PL measurement at 4.2 and 120 K. It is also seen from this figure that the peak energy measured at 300 K by PL measurement is lower compared to 4.2 and 120 K. For a fixed hole density, the peak energy shifted to lower energy with increasing PL measurement temperature can be seen from Fig. 8. It is very difficult to extract the exact band gap shift from the PL spectra because of life time broadening effects [36]. We determined the band gap, $E_g$ (Fig. 9) 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 [9]. This method was used by several authors for determination of $E_g$.

Fig. 10 (a) shows the band gap shrinkage of Zn-doped GaAs in the range of $4.5 \times 10^{17}$–$1.5 \times 10^{20}$ cm$^{-3}$, as a function of hole concentration. In this figure, we have also plotted the reported results for Zn, Be, and C doped GaAs measured at temperatures between 4.2 and 77 K, as the band gap shrinkage is independent of temperature [9,20]. The measured band gap shrinkage of carrier concentration of Be, C, and

![Fig. 4. Growth rate versus reciprocal of growth temperature.](image-url)
Zn-doped GaAs, exhibited consistent agreement between each other [9,14,18,24,25,28,37]. Fig. 10 (b) shows the band gap shrinkage of our results at the temperature ranges from 4.2 to 300 K. In general, the band gap shrinkage is proportional to the hole concentration of the form $p^{1/3}$, thus it can be represented by

$$\Delta E_g = E_g(\text{doped}) - E_g(\text{pure}) = - B p^{1/3}$$  \hspace{1cm} (7)

where $B$ has been adjusted to give the measured value of $E_g$ at higher hole concentrations and the minus sign signifies the band gap shrinkage at higher concentrations. The empirical relation for band gap narrowing with our data at 4.2 K can be written as

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

where $\Delta E_g$ 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 [38],

$$E_g = E_g(0) - \Delta E_g(p)$$  \hspace{1cm} (9)

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 $9.83 \times 10^{-9}$, $3.9 \times 10^{-7}$, and $3.9 \times 10^{-12}$, respec-
Fig. 10. (a). The band gap shrinkage of Zn-doped GaAs epilayers as a function of hole concentration. (b). The band gap shrinkage of Zn-doped GaAs epilayers as a function of hole concentration with different PL measurement temperatures. 

Fig. 11. 4.2 K PL spectra of Zn-doped GaAs epilayers as a function of TMGa flow rate.
and the main peak is shifted to lower energy with increasing TMGa mole fractions. This can be explained as, for a fixed growth temperature and mole fraction of DMZn, the hole concentration increases linearly with increasing growth rate [8]. At high growth rates, the deposited zinc is absorbed into the epilayer before it can be evaporated from the surface. At lower growth rates, however, the Zn atoms diffuse to the surface, where they can evaporate. Thus, as the growth rate is increased, the residence time of Zn required for incorporation decreases, leading to increased Zn concentration via reduced Zn re-evaporation. Therefore, the increase in hole concentration with increasing TMGa partial pressure, the PL peak shifted to lower energy with TMGa and hence higher band gap narrowing.

4. Conclusions

Zn-doped GaAs epitaxial layers grown by low pressure metal organic chemical vapor deposition technique in the hole concentration range $1 \times 10^{17}$ to $1.5 \times 10^{20}$ cm$^{-3}$ have been investigated by low temperature photoluminescence as a function of hole concentration and PL measurement temperatures, between 4.2 and 300 K. From the PL spectra we have obtained an empirical relation for FWHM, peak energy and band gap shrinkage as a function of hole concentration. These relations are considered to provide a useful tool for determining the hole concentration by low temperature PL measurement. The donor-to-acceptor (e-A) peak shifts to low energy side as the hole concentration increases. The (e-A) peak shifts to lower energy side as the TMGa mole fraction increases due to the lowering of Zn residence time. The surface morphology of Zn-doped GaAs is strongly dependent on the substrate surfaces below 600°C. The growth temperature affects the Zn-incorporation efficiency and a mirror smooth surface of having hole concentration $1.5 \times 10^{20}$ cm$^{-3}$ at 600°C was obtained.

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