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The near infrared photoluminescence of epitaxial $Ga_{0.5}In_{0.5}P$

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Abstract

The 1.17, 0.99 and 0.85 eV photoluminescence emission in $Ga_{0.5}In_{0.5}P$ epilayers grown on GaAs substrates by metal-organic chemical vapor deposition have been observed. Only the 1.17 eV emission depends on the ordered structure of $Ga_{0.5}In_{0.5}P$. A detailed study of the 1.17 eV emission has been made at various temperatures and excitation intensities. The 1.17 eV emission is interpreted as arising from the recombination of the donor–acceptor pair (DAP), composed of a silicon donor on the gallium sublattice site and a gallium vacancy acceptor as the nearest neighbor. The relationship between the ordered structure and the recombination energy of DAP is examined and a new energy equation for DAP transition is deduced.

1. Introduction

Various epitaxial techniques have been utilized for growing ternary alloy $Ga_xIn_{1-x}P$ ($GaInP_2$), matched to GaAs at $x \sim 0.5$, because of its usefulness in optoelectronics and electronic devices.

The spontaneous growth-induced ordering in $GaInP_2$ epilayers grown by metal-organic chemical vapor deposition (MOCVD) and metal-organic vapor-phase epitaxy (MOVPE) has been observed. Gomyo et al. [1] have given evidence that the anomalously low band-gap is related to the ordered structure of these epilayers. This type of ordering has a Cu–Pt-like structure, i.e. there exist alternate Ga-rich and In-rich planes in the column III sublattice along the (1 1 1) and (1 $\bar{1}$ 1) crystal directions. The degree of ordering of Ga and In atoms in the $GaInP_2$ epilayers can be controlled by varying the growth conditions [2–4]. This ordering effect, which lowers the band-gap energy, has obvious effects on the electric and optical properties of $GaInP_2$ epilayers [5].

Goetz [6], Yu [7] and Calleja et al. [8] demonstrated that carbon is the common residual contaminant in the materials grown by MOCVD and MOVPE because of the use of the trimethyl gallium.

Visser et al. [9] considered the broad photoluminescence (PL) emission with energy 1.3 eV as a donor–acceptor pair (DAP) transition of Si_{Ga}–V_{Ga}, where Si_{Ga} is a silicon donor on a gallium sublattice site and V_{Ga} is a gallium vacancy acceptor, in Si-doped $Ga_xIn_{1-x}As$ epilayers grown by MOCVD.

In this work, we studied the near infrared photoluminescence (NIPL) in $GaInP_2$ epilayers grown on GaAs substrates by MOCVD with respect to temperature and excitation intensity variations. We

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observed three peaks with energies 1.17, 0.99 and 0.85 eV and interpreted the 1.17 eV PL emission as the recombination of the DAP, composed of the silicon donor on the gallium sublattice site and the gallium vacancy acceptor because of the presence the silicon contamination in the $GaInP_2$ samples. We also examined the correlation between the ordering effect and the recombination energy of the DAP and derived a new energy equation for DAP transition.

2. Experimental

The 2 μm-thick $GaInP_2$ epilayers used for the present experiments were grown by MOCVD on the semi-insulating (1 0 0) GaAs substrates misorientated 3–5° towards one of the (1 1 0) directions. They were grown at various growth temperatures with a V/III ratio of 30. The lattice mismatch between $GaInP_2$ epilayer and GaAs substrate was less than $\pm$ 0.1%. The temperature- and excitation intensity-dependent NIPL spectra of $GaInP_2$ epilayers, grown at the substrate temperatures of 700°C and 650°C, were obtained with an ordinary grating monochromator and were detected by a liquid-nitrogen-cooled Ge detector using conventional lock-in techniques. Luminescence was excited with the 632.8 nm line of a He–Ne laser. The excitation intensity was 10^{-2}–10^{2} W/cm^2.

3. Results and discussion

3.1. NIPL and DAP PL

Fig. 1 shows the NIPL spectra of $GaInP_2$ epilayers grown at the substrate temperatures of 700°C (sample 1 with band-gap 1.86 eV) and 650°C (sample 2 with band-gap 1.83 eV), obtained at 77 K and with an excitation intensity 0.4 W/cm^2.

NIPL spectra of these two samples can be fitted adequately by a sum of three Gauss-type curves, where the three peaks are labelled as A, B and C. The three peak energies are 1.17, 0.99 and 0.85 eV in sample 1, and 1.14, 0.99 and 0.85 eV in sample 2. As shown in Figs. 1(a) and (b), the peak A moves from 1.17 to 1.14 eV with decreasing the growth temperature of $GaInP_2$ from 700°C to 650°C at the constant excitation intensity. The 30 meV shift of the peak A in samples 1 and 2 is just about equal to the band-gap energy difference of these two samples. However, the peak energies of B and C are independent of the sample growth temperatures, i.e. independent of varying degree of ordering in $GaInP_2$.

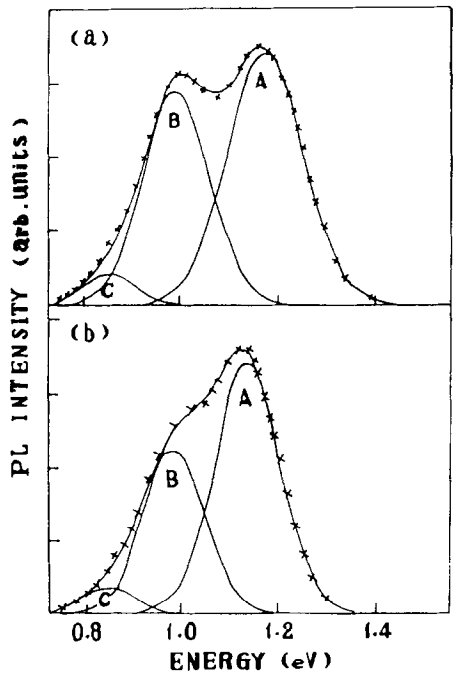

Fig. 1. NIPL spectra of $GaInP_2$ samples at excitation intensity 0.4 W/cm^2. (a): sample 1, grown at 700°C; (b): sample 2, grown at 650°C; x: experimental points.

Fig. 2 shows the NIPL spectra of sample 1 at various temperatures. At T = 77–150 K the NIPL spectra are mainly due to peaks A and B, but at T = 160–200 K the peak B becomes dominant. At temperatures higher than 200 K peak A disappears, that is, the 1.17 eV PL emission is quenched thermally. Fig. 3 shows the variation of PL intensity with temperature for the 1.17 eV PL emission in sample 1. From the above experimental data an activation energy of ΔE = 0.17 eV for the thermal quenching process of the 1.17 eV emission was obtained from the equation

$$I = C\exp(\Delta E/kT), \quad (1)$$

where I is the PL intensity and C a constant.

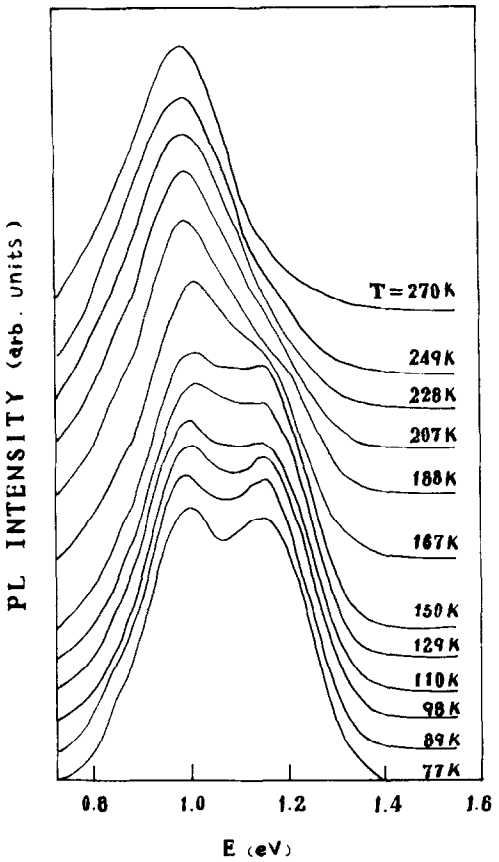

Fig. 2. NIPL spectra of sample 1 at various temperatures.

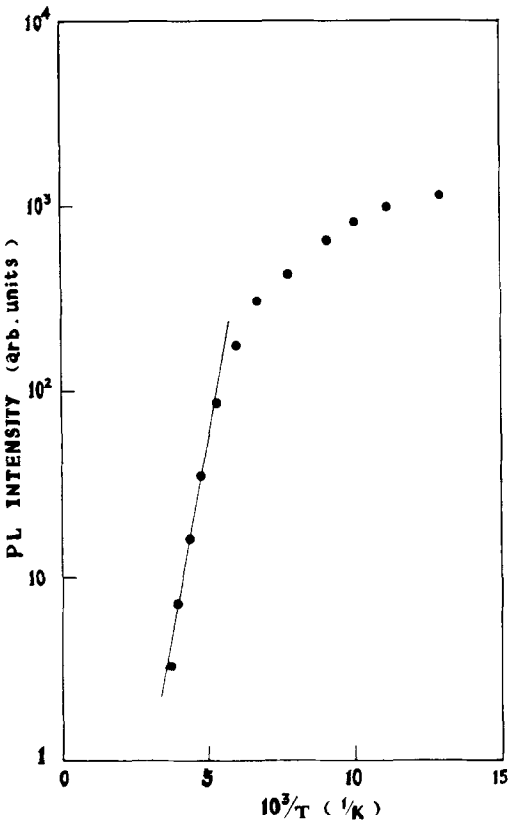

Fig. 3. PL intensity of 1.17 eV PL emission in sample 1 versus $10^3/T$ relation.

Fig. 4 shows the variation of the full width at half maximum (FWHM) of the 1.17 eV PL emission in sample 1 with the square root of the temperature. According to the configuration coordinate model [10], the theoretical temperature dependence of the FWHM $W(T)$ is

$$W(T) = (8 \ln 2)^{1/2} S^{1/2} \hbar\omega \, (\coth \hbar\omega/2kT)^{1/2}, \quad (2)$$

where $\hbar\omega$ is the longitudinal-optical-phonon energy and S is Huang–Rhys factor which characterizes whether the electron–phonon coupling is strong ($S \gg 1$) or weak ($S \ll 1$). Eq. (2) has been fitted to the experimental values in Fig. 4, and we obtained the values of $\hbar\omega = 31$ meV and $S = 5.3$. A Huang–Rhys factor, $S \gg 1$, indicates that in $GaInP_2$ epilayers there exists a strong electron–lattice coupling, which causes the 1.17 eV PL emission to have a very broad, Gaussian line shape (FWHM $\sim$ 0.17 eV at liquid nitrogen temperature) without any fine structure. The Frank–Condon shift Δ_{FC} is given by $\Delta_{FC} = S\hbar\omega = 0.16$ eV. Thus, the configuration coordinate diagram for 1.17 eV PL emission is shown in Fig. 5.

Fig. 6 shows the 77 K NIPL spectra as a function of excitation intensity for sample 1. At low excitation intensities there exist two strong peaks, A and B, and one weak peak C. With increasing the excitation intensity, peak A becomes dominant and peaks B and C disappear. The dependence of the 77 K NIPL intensity on the excitation intensity for sample 1 is shown in Fig. 7. For peak A, a linear relationship exists between the excitation intensity and the NIPL intensity but the NIPL intensities of peaks B and C appear to saturate with increasing excitation intensity. Fig. 8 shows the excitation intensity dependence of the peak energy and

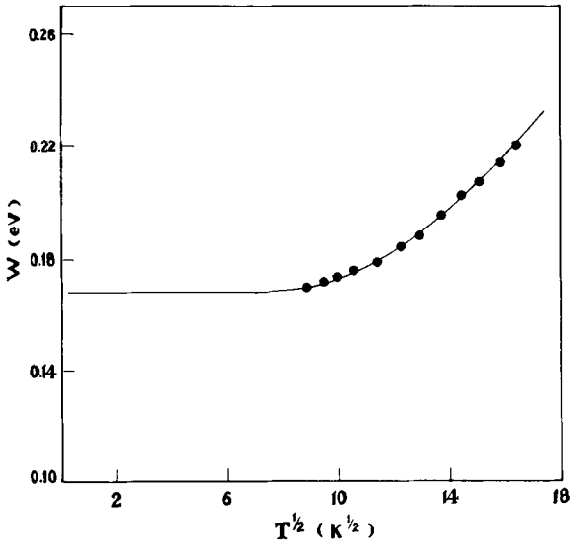

Fig. 4. Variation of FWHM of 1.17 eV PL emission in sample 1 versus $T^{1/2}$.

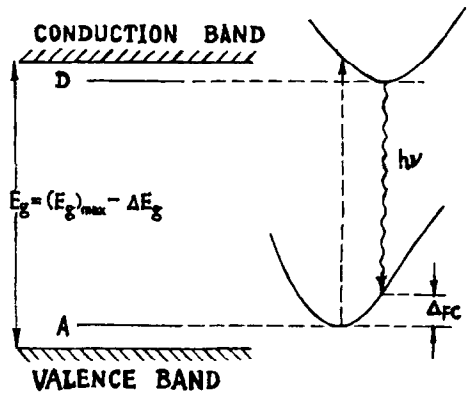

Fig. 5. The configuration coordinate diagram for 1.17 eV PL emission in sample 1.

FWHM of peak A in the NIPL spectra for sample 1. The peak energy shifts per decade of the excitation intensity change for peaks A, B and C are 4, 9 and 10 meV, respectively.

Because the second ion mass spectra of the $GaInP_2$ samples in question demonstrated that there exist the contaminants Si, Se and Zn and Visser et al. [9] considered the broad PL emission with energy 1.3 eV as a transition of Si_{Ga}–V_{Ga} DAP in Si-doped $Ga_xIn_{1-x}As$ epilayers, we considered the 1.17 eV PL emission as a PL emission of

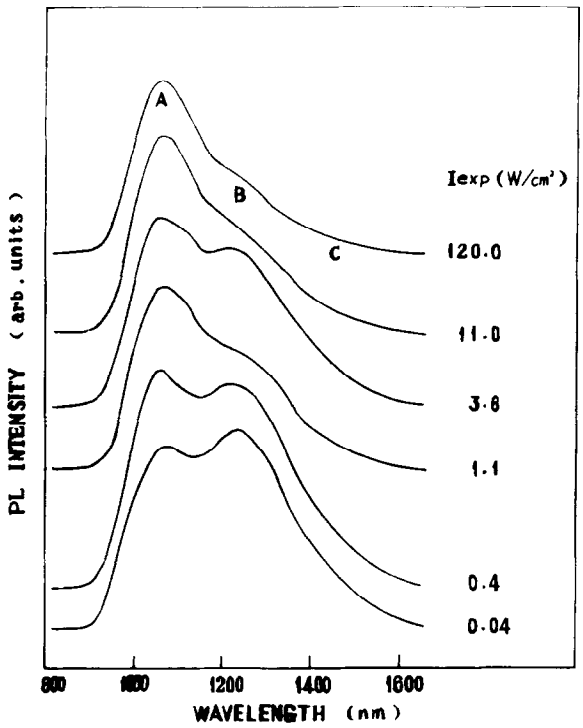

Fig. 6. 77 K NIPL spectra of sample 1 as a function of excitation intensity.

Si_{Ga}–V_{Ga} DAP. This is supported by some of its characteristics: the 0.17 eV FWHM, the 200 K thermal quenching temperature, the 4 meV peak energy shift per decade of the excitation intensity change, the strong electron–lattice coupling and the linear relationship between the excitation intensity and both the PL intensity and the PL FWHM.

The 0.99 eV band is due to the transition from a level of the phosphorus vacancy to the valence band [11,12] and the 0.85 eV PL emission is attributed to the transition from a hole trap to the valence band, where the hole trap is associated with structural defects created by the strain relaxation related to the lattice mismatch in $GaInP_2$ epilayers [13].

3.2. *Correlation between the DAP PL and the ordered structure*

Now we examine the correlation between the ordering effect and the recombination energy of

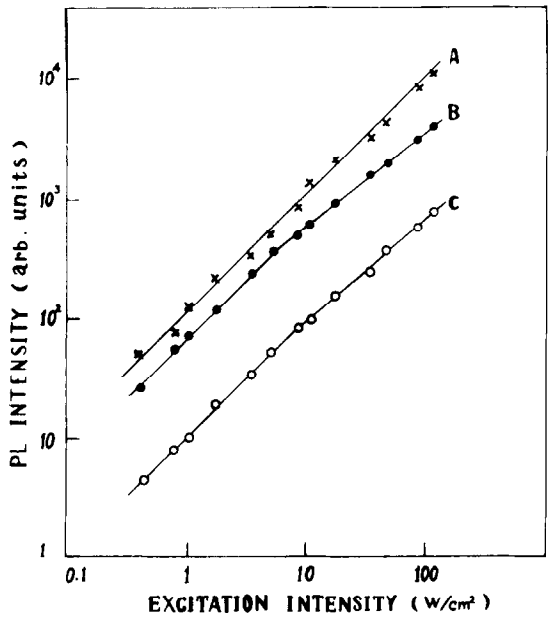

Fig. 7. Excitation intensity dependence of 77 K NIPL intensity of sample 1.

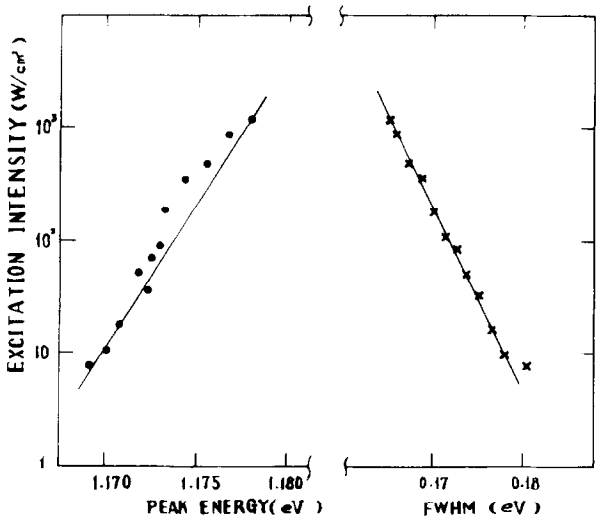

Fig. 8. Excitation intensity dependence of the peak energy and FWHM of peak A in 77 K NIPL spectra of sample 1.

DAP. As shown in Fig. 1, peak A, which has been identified as a DAP PL emission, moves from 1.17 to 1.14 eV with decreasing the growth temperature of $GaInP_2$ epilayers from 700°C to 650°C at constant excitation intensity. The 30 meV shift of the peak A in samples 1 and 2 is just equal to the band-gap energy difference of these two samples. This indicates that the DAP transition is dependent on the ordered structure in the $GaInP_2$ epilayers, and so, in the energy equation of the DAP transition the shift of the band-gap energy related to the ordered structure should be taken into account. Thus, the expression of the recombination energy $h\nu$ of DAP luminescence [7] is revised as follows:

$$h\nu = (E_g)_{max} - (E_d + E_a - e^2/\varepsilon_0 r) - \Delta_{FC} - \Delta E_g, \quad (3)$$

where $(E_g)_{max}$ is the band-gap energy in the disordered phase, E_d and E_a are the isolated donor and acceptor binding energies, respectively, $-e^2/\varepsilon_0 r$ is the Coulomb interaction energy of the DAP, Δ_{FC} is the Frank–Condon shift and ΔE_g is the shift of the band-gap energy related to the transition from the partially ordered to the disordered phase (see Fig. 5). Eq. (3) is a new energy equation for the DAP transition in the ordered structure.

4. Conclusions

In this work the NIPL for $GaInP_2$ epilayers was studied and a possible identification for the DAP is proposed. The correlation between the ordering effect and the recombination energy of DAP transition was examined and a new energy equation for DAP transition proposed.

Acknowledgements

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