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Correlation between deep-level photoluminescence and ordered structure in $Ga_{0.5}In_{0.5}P$ epilayers

JIACHANG LIANG
Department of Basic Sciences, Civil Aviation Institute of China, Tianjin 300300, People's Republic of China

YING GAO, JIALONG ZHAO
Changchun Institute of Physics, Chinese Academy of Sciences, Changchun 130021, People's Republic of China

Various epitaxial techniques have been utilized for growing ternary alloy $Ga_xIn_{1-x}P$, matched to GaAs at $x \approx 0.5$, because of its usefulness in optoelectronics and electronic devices. Spontaneous growth-induced ordering in $Ga_xIn_{1-x}P$ epilayers grown by metal–organic chemical vapour deposition (MOCVD) has been observed. Gomyo *et al.* [1] gave evidence that the anomalously low bandgap is related to the ordered structure of this alloy. This type of ordering has a CuPt-like structure, i.e. alternating Ga- and In-rich planes exist in the column III sublattice along the $(\bar{1}11)$ or $(1\bar{1}1)$ crystal direction, as shown in Fig. 1. The degree of ordering of Ga and In atoms in $Ga_xIn_{1-x}P$ epilayers can be controlled by varying the growth conditions [2–4]. This ordering effect, which lowers the bandgap energy, has an obvious influence on the electronic and optical properties of $Ga_xIn_{1-x}P$ epilayers.

In this study we examined the correlation between the ordering effect and the recombination energy of the donor–acceptor pair (DAP) in the near-infrared photoluminescence (NIPL) related to deep levels present in $Ga_xIn_{1-x}P$ epilayers grown on GaAs substrates by MOCVD, revise the energy equation for DAP transition and estimate the energy of DAP in the superlattice potential field, induced by the ordered structure in $Ga_xIn_{1-x}P$ epilayer.

Samples of $Ga_{0.5}In_{0.5}P$ epilayers with varying degrees of column III sublattice ordering, lattice-matched to GaAs substrates, were grown by MOCVD [5]. The temperature- and excitation intensity-dependent NIPL spectra of these samples were obtained with an ordinary grating monochromator and were detected by a liquid-nitrogen-cooled Ge detector using lock-in techniques. Luminescence was excited with 632.8 nm line of an He–Ne laser.

The 77 K NIPL spectra of these two samples can be fitted adequately by a sum of three Gaussian-type curves, as shown in Fig. 2, where the three peaks are labelled A, B and C, respectively. The three peak energies were 1.17, 0.99 and 0.85 eV in sample 1, and 1.14, 0.99 and 0.85 eV in sample 2. We have identified that peak A corresponds to a transition of DAP, composed of carbon donor on the gallium sublattice site and the next-nearest neighbour gallium vacancy acceptor, in terms of the transition energy, the full width at half-maximum, the thermal quenching temperature, the lineshape, the strong electron–lattice coupling, the peak energy shift rate

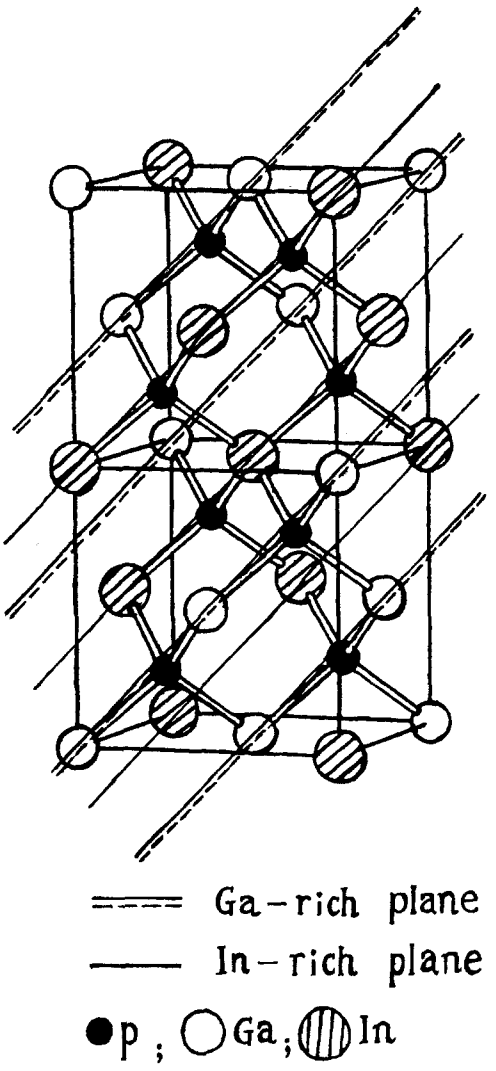

Figure 1 Fully ordered structure of $Ga_{0.5}In_{0.5}P$ epilayer. Ga atoms and In atoms are, respectively, on Ga- and In-rich planes.

and the linear relationship between excitation intensity and NIPL intensity [6], peak B is due to the transition from a level of the phosphorus vacancy to the valence band [7, 8], and peak C is attributed to the transition from a hole trap to the valence band [9].

As shown in Figs 1a and b, peak A moves from 1.17 to 1.14 eV with decreasing growth temperature of $Ga_{0.5}In_{0.5}P$ from 700 to 650 °C at constant excitation intensity. The 30 meV shift of peak A in samples 1 and 2 is equal to the bandgap energy

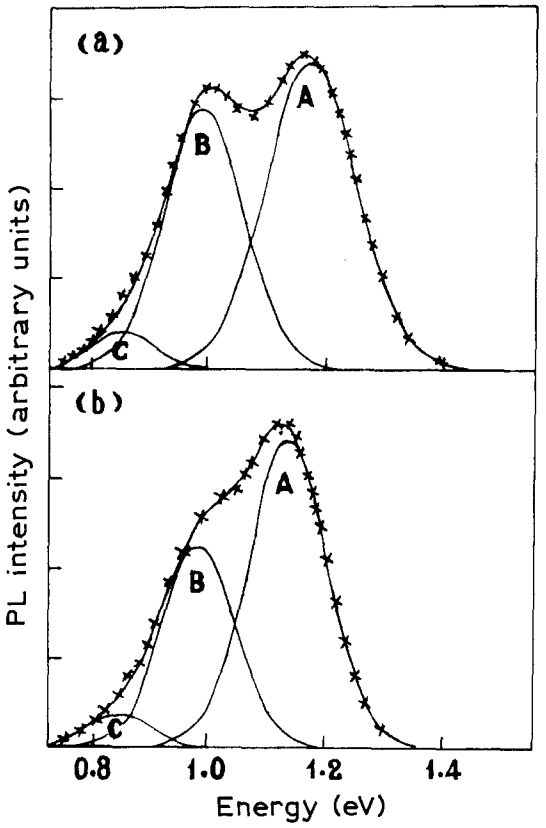

Figure 2 77 K NIPL spectra of $Ga_{0.5}In_{0.5}P$ samples at an excitation intensity 0.4 W cm^{-2}: (a) sample 1, grown at 700 °C, and (b) sample 2, grown at 650 °C; (×) experimental points.

difference of these two samples. This indicates that the DAP transition is dependent on the ordered structure in $Ga_{0.5}In_{0.5}P$ epilayers, and therefore the energy, E_s(DAP), of the DAP in the superlattice potential field, induced by the ordered structure, should be taken into account. Thus, the expression for the recombination energy $h\nu$ of the DAP luminescence [10] is revised as follows:

$$h\nu = E_g - (E_d + E_a - e^2/\varepsilon_0 r) - \Delta_{FC} - E_s(\text{DAP})$$

where E_g is the bandgap energy under conditions of the group III atoms on the column III sublattices becoming randomly distributed, 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} the Frank–Condon shift [6] and E_s(DAP) the energy of the DAP in the potential field induced by the ordered structure (Fig. 3).

We have demonstrated that the partially ordered structure of $Ga_xIn_{1-x}P$ epilayers leads to compositional modulation, which can be expressed by $(Ga_{x+\eta}In_{1-x-\eta}P)(Ga_{x-\eta}In_{1-x+\eta}P)$, where $\eta = x(0.5 - \varepsilon)$ and the ordering factor ε is determined by X-ray diffraction data for the $Ga_xIn_{1-x}P$ epilayer. For example, the compositional modulation of $Ga_{0.5}In_{0.5}P$ epilayer with bandgap energy 1.83 eV can be expressed as $(Ga_{0.55}In_{0.45}P)(Ga_{0.45}In_{0.55}P)$ [11]. By using a suitable superlattice potential to simulate the compositional modulation and using the electron–heavy-hole pair with suitable effective masses as a substitute for the DAP, it is possible to estimate the energy E_s(DAP) with a Kronig–Penney model.

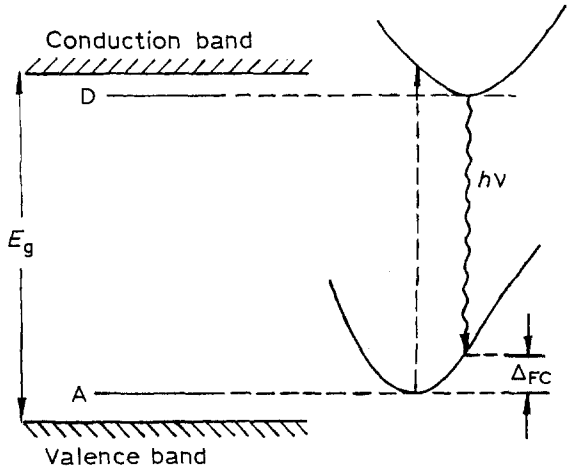

Figure 3 Schematic diagram of energy levels of DAP luminescence in $Ga_xIn_{1-x}P$ epilayers.

Using the electron–heavy-hole pair with $m_e^* = 0.087$ and $m_{hh}^* = 0.47$ instead of the DAP and using the superlattice potential with 6 nm-wide well and 6 nm-wide barrier instead of the compositional modulation induced by the partially ordered structure of $Ga_{0.5}In_{0.5}P$ epilayer, Gavrilovic *et al.* [12] estimated the energy E_s(DAP) to be 25 meV with a Kronig–Penney model. The value is in agreement with the 30 meV shift of peak A shown in Fig. 2.

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