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Temperature dependence of the photoluminescence of Zn-doped In_{0.32}Ga_{0.68}P grown on GaAs_{0.61}P_{0.39} substrates

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The photoluminescence (PL) spectra of Zn-doped In_{0.32}Ga_{0.68}P epitaxial layers grown on GaAs_{0.61}P_{0.39} substrates by liquid-phase epitaxy has been investigated in the temperature range of 8–300 K. The radiative recombination processes of the direct In_{0.32}Ga_{0.68}P alloys for which the composition is near the direct-indirect band gap crossover point have been studied at various temperatures. At higher temperatures (> 150 K) only one emission band corresponding to free-electron-to-free-hole transition dominates. Two peaks and one broad band are observed in the PL spectrum when the temperature is below 100 K. The peak denoted by A is due to direct interband radiative recombination. The temperature dependence of the band gap in In_{0.32}Ga_{0.68}P layers can be expressed as 2.25 – [1.79 × 10^{-3} T^2/(T + 1236)] eV. The peak denoted by B, exhibited by undoped or moderately Zn-doped (p ≤ 3 × 10^{16} cm^{-3}) InGaP samples, is attributed to the conduction-band-to-acceptor transition. A third broad band (C) dominates at low temperatures. The maximum shifts toward shorter wavelengths as the temperature is further lowered. It is the indirect donor-acceptor pair recombination from the unidentified deep donor levels associated with indirect X_c minima via Zn acceptor levels.

I. INTRODUCTION

One of the major topics in the field-of-light sources is the development of visible light-emitting devices for application to displays, high-density optical disks, bar-code readers, and transmitters in plastic optical fibers. Shorter wavelength laser operation is advantageous for obtaining small focused spots and highly luminous light sources for human vision.

The In_{1-x}Ga_xP ternary compound semiconductor has received increased attention recently due to its large direct band gap up to 2.26 eV (x ~ 0.74) at 300 K. This makes InGaP a potentially efficient spontaneous or stimulated emission source of radiation up to the green portion of the visible spectrum. It can be grown on commercial GaAs_{0.61}P_{0.39} epitaxial substrate with exact lattice match at a composition of 68% GaP and a band gap of about 2.17 eV (570 nm in wavelength). It is also a key material for AlInP/InGaP/AlInP, InGaP/AlInGaP/InGaP, InGaP/InGaAsP/InGaP, and InGaP/AlGaAsP/InGaP heterostructure visible laser systems. Although bright and efficient p-n junction luminescence has been highly expected for these material systems, the photoluminescence (PL) processes in acceptor doped or diffused In_{1-x}Ga_xP have received little scrutiny. Williams et al. observed the Zn acceptor-unknown donor pair emission of 2.1 eV at 77 K dominates for alloys with x > 0.7. Ermakov et al. reported the 77-K cathodoluminescence (CL) properties from the In_{1-x}Ga_xP_{0.51} (x = 0.6–0.8, z = 0–0.2) epitaxial layers with a hole concentration of 1 × 10^{17} cm^{-3}. Kato et al. investigated the 77-K CL processes from the solution grown Zn-doped In_{1-x}Ga_xP crystals (0.6 < x < 0.9) with the hole concentration range of 10^{17}–10^{18} cm^{-3}. However, detailed studies of the emission spectra over a broad temperature range in the In_{0.32}Ga_{0.68}P material with well-controlled acceptor dopants have not been reported.

In this paper, we report the temperature dependence of photoluminescence from Zn-doped In_{0.32}Ga_{0.68}P layers with various doping concentrations. Various luminescence bands involving donors and acceptors are identified, and ionization energy values are deduced from the data.

II. EXPERIMENT

In_{1-x}Ga_xP epitaxial layers were grown by liquid-phase epitaxy (LPE) using a graphite slider boat. The substrates were GaAs_{0.61}P_{0.39} commercial epitaxial wafers grown by vapor-phase epitaxy (VPE) on a Si-doped (100) GaAs substrates 2° off towards (110). A ~30-μm-thick graded composition of GaAsP layer is used between GaAs and GaAs_{0.61}P_{0.39} layer to avoid large lattice mismatch. The surface GaAs_{0.61}P_{0.39} layer is 40-μm thick and n doped to 7 × 10^{16} cm^{-3} with Te. The In melt was first baked at 900°C in a purified H_2 flow of 500 c.c./min for 10 h. After the baking process, 20.2 mg of InP and 12.7 mg of GaP, both polycrystalline, and an appropriate amount of Zn dopant were added to a 3-g In melt to form the growth solution with a liquidus temperature of 810°C. In order to control the hole concentration accurately, In–1%–Zn wires were used in our study. The doped epitaxial layers were grown by means of supercooling technique with 9–12°C supersaturation, which is the best growth condition determined previously. The thickness of InGaP epitaxial layers grown during a fixed growth period of 5 min was typically 4 μm.

The hole concentration of the Zn-doped InGaP layers was measured by the capacitance–voltage (C–V) method. The Schottky barrier was formed with liquid-mercury...
TABLE I. 300-K electrical and optical properties of the Zn-doped In$_{0.32}$Ga$_{0.68}$P samples used in this study.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>$\rho$ (\times 10^{16} \text{cm}^{-3})</th>
<th>PL peak energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>REF</td>
<td>undoped, $n$ type, $n = 1.0 \times 10^{16}$</td>
<td>2.1618</td>
</tr>
<tr>
<td>Zn-1</td>
<td>0.3</td>
<td>2.1595</td>
</tr>
<tr>
<td>Zn-2</td>
<td>1.0</td>
<td>2.1558</td>
</tr>
<tr>
<td>Zn-3</td>
<td>5.0</td>
<td>2.1540</td>
</tr>
<tr>
<td>Zn-4</td>
<td>8.0</td>
<td>2.1520</td>
</tr>
<tr>
<td>Zn-5</td>
<td>30</td>
<td>2.1580</td>
</tr>
<tr>
<td>Zn-6</td>
<td>50</td>
<td>2.1573</td>
</tr>
</tbody>
</table>

metal by a mercury-probe station. The PL measurement was performed using argon-ion laser excitation (4880-Å line) with an average power density of $\sim 5$ W/cm$^2$ and a spot size of $\sim 1$ mm in diameter. The emission spectra were analyzed by a 1-m spectrometer and detected with a silicon pin photodetector. The samples were mounted on a holder inside a cryostat and the temperature was varied and controlled by a thermalfoil heater wound near the holder and detected by a Pt temperature sensor.

### III. RESULTS

Table I illustrates some of the room-temperature electrical and optical properties of Zn-doped In$_{0.32}$Ga$_{0.68}$P epitaxial layers used for this investigation. The undoped ($n$ type) In$_{0.32}$Ga$_{0.68}$P sample with a background concentration of $1 \times 10^{16}$ cm$^{-3}$ is used as a reference for the PL measurements. At room temperature, only one emission band due to the recombination of free electrons and free holes is observed for the Zn-doped InGaP layers, as seen from the emission band due to free-electron-to-free-hole transition in the undoped InGaP layers. The PL spectra at 100 K of all the samples illustrated in Table I are shown in Fig. 1. These spectra are normalized to the same main peak intensity. Except for the undoped and most highly doped samples REF and Zn-6, respectively, as shown in Figs. 1(a) and 1(g), all other samples exhibit two peaks and one broad band denoted as $A$, $B$, and $C$. Peak $A$ has the narrowest full width at half maximum (FWHM) and the highest photon energy which is the same as that observed in the undoped sample. The lower energy peak $B$, located about 30–50 meV below peak $A$, moves closer to peak $A$. The $B$-peak intensity increases with increasing the hole concentration. At hole concentrations higher than $3 \times 10^{17}$ cm$^{-3}$, these two peaks, $A$ and $B$, merge with each other. The wide band $C$ is located at 130–150 meV below peak $B$.

Figure 2(a) presents the temperature dependence ($T = 8$ – 150 K) of emission spectra from the sample Zn-1 with a hole concentration of $3 \times 10^{16}$ cm$^{-3}$. No significant changes take place when the temperature is lowered from 300 to 120 K, as in the case of undoped InGaP layer. Peak $B$ starts to emerge as a shoulder of peak $A$ in the low-energy side at 100 K and its relative intensity gradually increases when the temperature is reduced. A decrease in the temperature below 50 K gives rise to a long-wavelength band $C$ which is located in the wing of peak $B$. The $C$-band intensity increases when the temperature is further decreased. At the same time, the band $C$ shifts rapidly toward shorter wavelength. The positions of peaks $A$ and $B$, however, hold almost constant at temperatures below 77 K.

The PL spectra of the samples Zn-2 and Zn-4 with a hole concentration of $1 \times 10^{17}$ and $8 \times 10^{16}$ cm$^{-3}$, respectively, at various temperatures between 8 and 220 K are shown in Figs. 2(b) and 2(c). The only one emission band dominates above 150 K as in the case of the lightly doped sample Zn-1. When the temperature is lowered to 100 K, these peaks $A$ and $B$ and the band $C$ are distinctly separate. As seen in Fig. 2(a), a decrease in the temperature moves the $C$-band maximum toward shorter wavelengths and peak $B$ becomes a wing of this band in the high-energy side. A further decrease in the temperature causes the merging band to dominate the spectrum and then the peak $A$ appears as a hump [e.g., 20-K spectrum of
FIG. 2. Photoluminescence spectra of Zn-doped In_{0.53}Ga_{0.47}P layers with $p = (a) 3 \times 10^{16}$ cm$^{-3}$, (b) $1 \times 10^{17}$ cm$^{-3}$, (c) $8 \times 10^{17}$ cm$^{-3}$, and (d) $5 \times 10^{18}$ cm$^{-3}$ at various temperatures between 8 and 220 K to show the gradual evolution of the peaks.

band C as a function of temperature for samples REF, Zn-1, Zn-2, Zn-4, and Zn-6. This figure also shows the temperature dependence of the full width at half maximum of peak A to compare with the theoretical value of 1.85 kT.

Fig. 2(b)] in the short-wavelength wing of this band or disappears [e.g., 20-K spectrum of Fig. 2(c)].

The temperature dependence of PL spectra from the sample Zn-6 with a hole concentration of $5 \times 10^{18}$ cm$^{-3}$ is shown in Fig. 2(d). At 100 K, we can observe a weak but very broad band C and a stronger and narrower peak located at 2.210 eV (~5610 Å), whose energy is between the peak A at 2.235 eV (~5550 Å) and peak B at 2.196 eV (~5650 Å) of the 100-K PL spectrum for the lightly doped samples. Similarly, the band C rapidly grows and becomes prominent with reduced temperature. At 8 K, the relative intensity of this merging peak located at 2.210 eV is too weak to be observed in this 8-K spectrum.

Figure 3 summarizes the variation of the photon energies of the peaks A and B and the band C as a function of temperature for samples REF, Zn-1, Zn-2, Zn-4, and Zn-6. This figure also shows the temperature dependence of the full width at half maximum of peak A to compare with the theoretical value of 1.85 kT.

IV. DISCUSSION

Peak A in Figs. 1 and 2 is attributed to the near band-to-band transition because of the sharpness of this peak and its peak position. The temperature dependence of the bandgap shown in Fig. 3 can be expressed as the Varshni equation:

$$E_g(T) = E_g(0) - \alpha T^2/(T + \beta),$$

where $E_g(0)$ is the energy gap at 0 K, $\alpha$ and $\beta$ are material constants. The calculated $E_g(0)$, $\alpha$, and $\beta$ by the least-square method are 2.25 eV, $1.79 \times 10^{-3}$ eV/K, and 1236 K, respectively. The temperature dependence of the FWHM of peak A is also shown in Fig. 3. The experimental value agrees well with the theoretical value of $1.85 kT$ (Ref. 14) (expected in the limit of negligible impurity broadening) as shown in Fig. 3, where $k$ is the Boltzmann constant. The slightly smaller FWHM than the theoretical value above 120 K seems to be due to reabsorption of emitted photons with energies higher than the peak energy by the epitaxial layer, while the somewhat larger FWHM at the temperatures below 60 K may be due to the existence of another radiative transition process such as residual-donor-to-valence-band recombination merging into the band-to-band transition peak.

This difference between peaks A and B, in the range 30–50 meV depending on the hole concentration, is in good agreement with the thermal ionization energy of solution grown polycrystalline Zn-doped In$_{1-x}$Ga$_x$P obtained from Hall measurements. This indicates that the peak B is a transition from the conduction band to the Zn acceptor level. When the temperature is lowered, the probability of liberation of nonequilibrium electrons from the conduction band to the acceptor level becomes much higher and consequently the relative intensity of peak B to peak A is increased. We can also deduce that the high-energy 2.210-eV peak as shown in Fig. 2(d) is merged with peaks A and B because of the evolution of acceptor impurity levels into a band and merging with the valence band.

At low temperatures, the band C is an asymmetric wide shape with an extended long-wavelength wing. We have investigated that the C-band maximum shifts to higher energies and the FWHM of band C decreases with an increasing excitation level. Therefore, the band C has the feature of donor-acceptor (D–A) pair recombination. It should also be pointed out that the PL spectrum of Zn-doped GaP has a band with the similar feature and it is usually attributed to radiative D–A pair recombination. Bachrach and Hakki and Ermakov et al. have reported that the emission transition of band C from the In$_{1-x}$Ga$_x$P samples with $x = 0.64-0.70$ is due to D–A pair emission by time-resolved spectroscopy. Ermakov et al. assumed that the band C is due to radiative recombination of electrons from residual deep donor levels (such as Si and S) associated with indirect $X_C$ valley in direct band gap alloys via Zn acceptor levels. The ionization energy of these donors has been reported as high as 65 meV.

The behavior of band C shown in Figs. 1 and 2 can be illustrated in terms of the model of Fig. 4. For illustration we show a schematic diagram of the bandstructure in the In$_{0.32}$Ga$_{0.68}$P alloys near the crossover but where the zone center conduction-band minimum is still lower than the indirect minima at $k = (1,0,0)$. Associated with the indirect minima is the unidentified donor. Now at 300 K the lowest electron state is the donor level at (1,0,0). Since the indirect recombination is slow and the $E_F-E_D$ separation is small enough so that the electrons can reach $\Gamma_0$, the dominant recombination is direct. As the temperature is lowered, the $\Gamma_0-X_C$ separation will be decreased (such as from 79 meV at 300 K to 65.5 meV at 77 K in the In$_{0.32}$Ga$_{0.68}$P alloy) but the band gap is still direct. The
When a donor and an acceptor impurity form a pair, the normal ionization energy $E_D$ (or $E_A$) of an isolated donor (or acceptor) is reduced due to the Coulombic interaction between the electron and the hole bound to the impurities. The recombination energy of pair-band luminescence is, therefore, given by the equation:

$$\nu = E_g - (E_D + E_A) + e^2/\varepsilon r$$

where $E_g$ is the band gap, $r$ is the separation between the impurities, and $\varepsilon$ is the dielectric constant. For substitutional impurities, the donors and acceptors in the pairs must be on lattice sites, so that the recombination energy of D–A pairs will be influenced by the $r$ values, especially for the direct but near the crossover composition or indirect alloys. When the temperature is lowered, the separation between the ionized donor and acceptor, $r$, will be decreased as in the case of the lattice-constant variation of the host material In$_{0.32}$Ga$_{0.68}$P due to its thermal coefficient of expansion. Consequently, the Coulombic interaction term will have much influence at low temperatures to cause a C-band shift toward the shorter wavelengths. The fact that no phonon replicas and fine pair lines as observed in the GaP compound can be resolved at low temperatures may be due to phonon broadening and the capability of PL resolution.

V. CONCLUSIONS

We have demonstrated the temperature dependence of the photoluminescence of the Zn-doped In$_{0.32}$Ga$_{0.68}$P materials with carrier concentrations of $3 \times 10^{16}$ to $5 \times 10^{18}$ cm$^{-3}$. At temperatures above 150 K, the band-to-band recombination dominates for all the samples. When the temperature is lowered to 100–77 K, there appear two peaks A and B and one broad band C in the PL spectra. The peak A is due to the band-to-band transition and the temperature dependence of band gap in In$_{0.32}$Ga$_{0.68}$P layers varies as $2.25 - [1.79 \times 10^{-3} T^2/(T+1236)]$ eV. The relative intensity of peak B increases with the hole concentration and we may attribute the peak to be the band-to-acceptor recombination. The band C has the feature of donor-acceptor pair recombination and becomes prominent at low temperatures ($< 50$ K). It is due to the transition from the deep donor (residual) level associated with indirect $X_C$ minima via Zn acceptor levels. The C-band maximum shifted toward shorter wavelengths at lower temperatures is due to the enhancement of the Coulombic interaction term between the Zn acceptors and unidentified deep donors.

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23 See Ref. 14, p. 314.