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Direct bandgap photoluminescence from n-type indirect GaInP alloys

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This work studies Te doping effects on the direct bandgap photoluminescence (PL) of indirect Ga\textsubscript{i-x}In\textsubscript{x}P alloys (0.72 ≤ x ≤ 0.74). The temperature-dependent PL shows that the energy difference between direct Γ valley and indirect X valleys is reduced due to the bandgap narrowing (BGN) effect, and the direct band transition gradually dominates the PL spectra as temperature increases. Carrier thermalization has been observed for Te-doped Ga\textsubscript{i-x}In\textsubscript{x}P samples, as integrated PL intensity increases with increasing temperature from 175 to 300 K. The activation energy for carrier thermalization is reduced as doping concentration increases. Both BGN effect and carrier thermalization contribute to the carrier injection into the Γ valley. As a result, the direct band transition is enhanced in the Te-doped indirect Ga\textsubscript{i-x}In\textsubscript{x}P alloys. Therefore, the PL intensity of the Ga\textsubscript{0.74}In\textsubscript{0.26}P sample with active doping concentration of 9 × 10\textsuperscript{17} cm\textsuperscript{-3} is increased by five times compared with that of a nominally undoped sample. It is also found that the PL intensity is degraded significantly when the doping concentration is increased to 5 × 10\textsuperscript{18} cm\textsuperscript{-3}. From cross-section transmission electron microscopy, no large dopant clusters or other extended defects were found contributing to this degradation. © 2017 Chinese Laser Press

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1. INTRODUCTION

Large bandgap Ga\textsubscript{i-x}In\textsubscript{x}P alloys have potential use for top junction in tandem solar cells and yellow-green light emitting diodes [1,2]. However, the Ga\textsubscript{i-x}In\textsubscript{x}P alloy becomes an indirect band alloy when its band energy is above 2.2 eV. At the direct–indirect band crossover, the Ga content of Ga\textsubscript{i-x}In\textsubscript{x}P is within a range between 0.69 and 0.72 [3]. Due to the weak luminescence emission, studies of the optical properties of Ga\textsubscript{i-x}In\textsubscript{x}P alloys near the direct–indirect band crossover and in the indirect band region are more challenging than for direct band alloys. In addition, the lack of lattice-matched substrates and ordering effects adds more complexity to the studies.

Previous studies have provided detailed information on the electronic structures of Ga\textsubscript{i-x}In\textsubscript{x}P alloys (0 ≤ x ≤ 1) [4,5]. The experimental results showed that the luminescence efficiency of Ga\textsubscript{i-x}In\textsubscript{x}P-based LED degrades significantly for emission wavelengths shorter than 590 nm (2.1 eV) [6]. Despite carrier confinement issues for large bandgap Ga\textsubscript{i-x}In\textsubscript{x}P alloys [7,8], a simplistic approach was developed to model the luminescence intensity degradation as a function of the energetic separation between direct and indirect bands [9]. Based on this model, as the Ga content x increases for direct band Ga\textsubscript{i-x}In\textsubscript{x}P to approach a larger bandgap energy, the energetic separation between the Γ and the X minima, $E_{\text{Γ}}(x) - E_{\text{X}}(x)$, becomes smaller. Because the density of states (DOS) of the X valley is about 10 times larger than that of the Γ valley of Ga\textsubscript{i-x}In\textsubscript{x}P (0 ≤ x ≤ 1), the probability of electrons occupying the indirect band minimum is high. Therefore, the luminescence efficiency drops exponentially for Ga\textsubscript{i-x}In\textsubscript{x}P alloys near the direct–indirect crossover, and indirect band Ga\textsubscript{i-x}In\textsubscript{x}P alloys have poor luminescence efficiency. Although the indirect band Ga\textsubscript{i-x}In\textsubscript{x}P alloys have large direct band energies, they are not suitable for light-emitting applications, as indirect band transitions dominate.

More recently, the concept of “pseudo-direct” bandgap has been developed for Ge by using tensile strain and high n-type doping to promote the direct-band transition [10]. The tensile strain reduces the energetic separation between Γ and L valleys in Ge, and carrier injection into the Γ valley was increased. The high n-type doping increased band filling in the L valleys to promote the thermal excitation of electrons into the Γ valley. As a result, strain and doping effects enhance the direct band transition in Ge. The direct band transition dominates the light emission at room temperature, and Ge-based LEDs and lasers
have been demonstrated [10,11]. For the indirect Ga$_{1-x}$In$_x$P alloys near the direct—indirect band crossover, n-type doping is also expected to enhance the direct band transition due to similar mechanisms.

In this paper, we study the n-type Te doping effects on the photoluminescence (PL) of indirect band Ga$_{1-x}$In$_x$P alloys. The energy difference between Γ and X valleys of the chosen Ga$_{1-x}$In$_x$P alloys in this study (0.72 ≤ x ≤ 0.74) is less than 40 meV. Temperature-dependent PL provides the basis for a detailed analysis of the doping effects on the electronic structure of the Te-doped Ga$_{1-x}$In$_x$P samples. This work is meant to explore the indirect Ga$_{1-x}$In$_x$P alloys for direct band light emission. This work also can be extended for other III–V alloys [Al$_x$In$_{1-x}$P, (Al$_x$Ga$_{1-x}$)$_{1-y}$In$_y$P, Al$_x$Ga$_{1-x}$As, etc.] with indirect bandgap or near the direct-indirect band crossover.

2. EXPERIMENTAL

The epitaxy of Ga$_{1-x}$In$_x$P films on Si (001) substrates off-cut 6° toward the [110] direction was carried out using an Aixtron Cirus metal-organic chemical vapor deposition (MOCVD) reactor, where trimethylgallium (TMGa), trimethylindium (TMIN), arsine (AsH$_3$), phosphine (PH$_3$), and diethyltellurium (DETe) were used as precursors. A compositionally graded Ge$_x$Si$_{1-x}$ buffer with a grading rate of 10% μm$^{-1}$ was used to reach lattice-matching conditions for the Ga$_{1-x}$In$_x$P films. The Ge$_x$Si$_{1-x}$-graded buffer was terminated with a 1 μm thick Ge$_{0.58}$Si$_{0.42}$ capping layer, which was closely lattice matched (mismatch <0.1%) to the Ga$_{1-x}$In$_x$P films. Then a chemical mechanical polishing (CMP) process was applied to remove the top 500 nm Ge$_{0.58}$Si$_{0.42}$ capping layer and planarize the surface. A 100 nm GaAs$_{0.55}$In$_{0.45}$ inter-layer was grown on the CMPed Ge$_{0.58}$Si$_{0.42}$ capping layer to initiate the III–V growth, which was also lattice matched to the Ga$_{1-x}$In$_x$P films. Details of the epitaxy of GaAs$_{1-y}$P$_y$ inter-layer on Ge$_x$Si$_{1-x}$ graded buffer on Si (001) can be found in Ref. [12]. A 400 nm Ga$_{1-x}$In$_x$P film was grown on GaAs$_{0.55}$In$_{0.45}$/Ge$_x$Si$_{1-x}$/Si at 650°C with a V/III ratio of 200. The effective flow rates of TMGa, TMIN, and PH$_3$ were 1.31, 0.69, and 400 sccm, respectively, which were the same for all growth runs of Ga$_{1-x}$In$_x$P films targeting a Ga content of 0.74. The tellurium was in situ doped during the epitaxy of the Ga$_{1-x}$In$_x$P films, and the effective flow rate of DETe was adjusted for each sample to introduce different Te-doping concentrations. Capacitance-voltage measurements showed that the active doping concentration, n, increased from 7 × 10$^{16}$ to 5 × 10$^{18}$ cm$^{-3}$, depending on the DETe flow rate. All Ga$_{1-x}$In$_x$P samples were pieces of the size of 2 cm × 2 cm.

X-ray diffraction (XRD) was used to measure the strain status and the compositions of the Ga$_{1-x}$In$_x$P films. Selective defect etching was used to estimate the etch pit density (EPD) of the Ga$_{1-x}$In$_x$P samples. The selective etching was carried out by pouring concentrated liquid H$_3$PO$_4$ (85 wt. %) into a glass crucible on a hotplate. The hotplate was then heated up and stabilized at the desired temperature of 250°C for 2 min [13]. The Ga$_{1-x}$In$_x$P samples were lowered into the hot H$_3$PO$_4$ for 10 s. The EPD was counted using a scanning electron microscope (SEM). Temperature-dependent PL measurements were conducted from 6 to 300 K using a 473 nm solid-state laser for excitation. The laser spot size was 4 × 10$^{-2}$ cm$^{-2}$, and the excitation power was 50 mW. The PL emission was detected using a Spex 750M spectrometer and a Hamamatsu thermoelectrically cooled GaAs photomultiplier tube (PMT).

3. RESULTS AND DISCUSSION

Our target Ga content was 0.74, and XRD measurements confirmed that there is a small tensile strain (0.1%–0.2%) in the undoped Ga$_{1-x}$In$_x$P films, and the Ga content was measured to be 0.735 ± 0.005. However, a composition change was observed for the n-type doped Ga$_{1-x}$In$_x$P sample with n = 2 × 10$^{18}$ cm$^{-3}$, where the Ga content was reduced to 0.720. The XRD results were consistent with secondary ion mass spectrometry measurements. The composition change was caused by the tellurium dopants acting as surfactant, which changed the gallium and indium incorporation into the crystal lattice [14]. In addition, XRD showed that the Ga content was 0.734 for the Ga$_{1-x}$In$_x$P sample with a doping level of n = 5 × 10$^{18}$ cm$^{-3}$. This suggests that the composition shift was not reproducible, which cannot be simply resolved by increasing the TMG flow to compensate for the Ga content reduction. In addition, due to the composition shift, strains varied from ~0.2% to 0.25% for Te-doped Ga$_{1-x}$In$_x$P samples with no clear correlation with Te-doping concentrations.

In Fig. 1(a), the [110]-pole transmission electron microscopy (TEM) pattern for a lightly Te-doped Ga$_{0.74}$In$_{0.26}$P sample (n = 7 × 10$^{16}$ cm$^{-3}$) shows only fundamental reflections, even for long exposure times. The absence of superlattice reflections indicates that the sample was fully disordered [15]. The absence of disorder is due to the high growth temperature of 650°C, which is similar to ~700°C reported in Ref. [16], effectively suppressing the ordering effect in Ga$_{1-x}$In$_x$P alloys. Furthermore, increased Te-doping concentration also reduces the ordering effect [17]. Therefore, the band energy distortion due to an ordering effect can be eliminated. Figure 1(b) shows the SEM image of the etch pits on the Ga$_{0.74}$In$_{0.26}$P film. The EPD was counted to be (3 ± 0.5) × 10$^6$ cm$^{-2}$, which indicates good epitaxy quality.

Temperature-dependent PL is well suited to evaluate materials with direct and indirect bandgap properties. For indirect bandgap semiconductors, the dominant low temperature (≤30 K) PL peak with the highest energy can be attributed.

Fig. 1. (a) [110]-pole TEM pattern of fully disordered lightly Te-doped Ga$_{0.74}$In$_{0.26}$P sample with n = 7 × 10$^{16}$ cm$^{-3}$. (b) SEM image of the etch pits of Ga$_{0.74}$In$_{0.26}$P film, and EPD = (3 ± 0.5) × 10$^6$ cm$^{-2}$.
to excitonic recombination, while the lower energy peaks are associated with phonon replica and donor-acceptor pair (DAP) recombinations. The excitonic recombination can overlap with band-to-band transitions at higher temperatures, where the band-to-band emission peaks show a redshift with increasing temperature [18]. Direct bandgap semiconductors, however, generally show dominant direct bandgap recombination at low temperatures, as the exciton binding energy is usually quite small [19]. At higher temperatures, the direct bandgap luminescence redshifts and the PL intensity decreases. In the case of an indirect bandgap semiconductor with small difference between direct and indirect bandgap transition, at low temperatures the PL spectrum look like that from an indirect bandgap material while at higher temperatures direct bandgap characteristics dominate [20]. Because the direct bandgap emission is fueled by thermalized electrons, the direct bandgap PL intensity increases with temperature, opposite to the direct bandgap semiconductor PL intensity [21].

According to these rules, the origins of PL emission peaks in indirect Ga$_{1-x}$In$_x$P samples can be identified. Three Te-doped Ga$_{1-x}$In$_x$P samples labeled as S01 ($n = 7 \times 10^{16}$ cm$^{-3}$), S02 ($n = 9 \times 10^{17}$ cm$^{-3}$), and S03 ($n = 2 \times 10^{18}$ cm$^{-3}$) were selected for detailed analysis of the doping effects on their optical properties. Figure 2 shows the temperature-dependent normalized PL spectra of these three samples. At a low temperature of 6 K, three major peaks are observed for each sample. The peak with the highest energy and the highest PL intensity was assigned to a non-phonon (NP$_x$) indirect transition from the X conduction band edge [3]. The measured separation energies between the second peak and the NP$_x$ peak for S01, S02, and S03 samples are 29, 22, and 23 meV, respectively. Then, the second peak was likely to be the longitudinal acoustic (LA$_x$) peak, with a calculated LA$_x$ phonon energy of 29 meV [3]. It should be noted that the experimental separation energies of S02 and S03 are several meV lower than the calculated LA$_x$ phonon energy. This could be caused by either composition change or the bandgap narrowing (BGN) effect [22]. As previously mentioned, we suspect a Ga composition change of 2% in Te-doped Ga$_{1-x}$In$_x$P samples. But this composition change would only cause a small change (~0.3 meV) in the phonon energy. Therefore, the Te-doping is likely to cause the reduction of the separation energy between NP$_x$ and LA$_x$. The broad third peak at low energy was assigned to a DAP emission. In Fig. 2(a), the NP$_x$ peak and the LA$_x$ peak gradually weaken and finally disappear at 80 K, while another peak at 2.31 eV appears at 100 K. This new peak starts to dominate the PL emission as temperature increases, as indicated by a red arrow. The peak position and its shift to a longer wavelength with increasing temperature indicates that this emission is due to the direct band recombination. The direct band recombination appears at 60 K in S02 mixing with the NP$_x$ and LA$_x$ peaks, as shown in Fig. 2(b). In Fig. 2(c), the direct band emission peak is inseparable from exciton and photon peaks. The peak broadening from 40 to 60 K indicates the appearance of direct band recombination, and the direct band recombination starts to dominate above 60 K.

Figure 3 shows the peak positions of the $\Gamma$ band transitions (squares), NP$_x$ lines (circles), and LA$_x$ lines (triangles) versus temperature for S01, S02, and S03. The stars present the $\Gamma$ peak positions deduced from Ref. [3], which show that the data points of the fully disordered lightly doped Ga$_{0.74}$In$_{0.26}$P sample (S01) are closely matched with the reported values. The separation energies between $\Gamma$ and X bands of S01 and S02 are 39 and 27 meV, respectively. In S02, relative to S01, the BGN effect lowered the peak energies of $\Gamma$, NP$_x$, and LA$_x$ by 31 ± 3, 21 ± 1, and 13 ± 2 meV, respectively. This shows that the doping-induced BGN effect is more significant for the $\Gamma$ band shift than for the X band shift. As a result, the separation energy between $\Gamma$ and X bands is reduced by

![Fig. 2. Temperature-dependent normalized PL spectra (6–300 K) of Te-doped Ga$_{0.74}$In$_{0.26}$P samples with (a) $n = 7 \times 10^{16}$ cm$^{-3}$, (b) $n = 9 \times 10^{17}$ cm$^{-3}$, and (c) $n = 2 \times 10^{18}$ cm$^{-3}$. The positions of NP$_x$, LA$_x$, and DAP emission peaks from Ref. [3] are labeled, and their positions are indicated by dashed black lines. Solid red lines and arrows indicate the positions of direct band emission, shifting with increasing temperature.](image1)

![Fig. 3. Peak positions of Te-doped Ga$_{0.74}$In$_{0.26}$P samples versus temperature. The data points marked with green stars are from Ref. [3]. Dashed lines are fitted to derive the thermal coefficients of the $\Gamma$ band.](image2)
coefficients of S01, S02, and S03 have similar values: in the temperature range from 100 to 300 K. The temperature are derived from linear regression fitting of the peak energies in the temperature range from 100 to 300 K. The temperature coefficients of S01, S02, and S03 have similar values: \(-3.68 \times 10^{-4}\), \(-3.32 \times 10^{-4}\), and \(-3.54 \times 10^{-4}\) eV/K, respectively. This indicates that the direct band transition dominates the PL spectra from 100 K upward in S03. Due to the BGN effect and the composition fluctuation, the band edges of Γ and X in S03 are very close (less than 10 meV).

Direct band materials, such as the Ga\(_x\)In\(_{1-x}\)P (x = 0.51) alloy, show a thermal quenching process, and its PL intensity decreases as temperature increases [23]. For the indirect Ga\(_x\)In\(_{1-x}\)P alloy, S01, the thermal quenching effect is not obvious, as shown in Fig. 4(a), and the PL spectra are weak. However, Figs. 4(b) and 4(c) show that PL intensities of both S02 and S03 increase with the increasing temperature, which are contrary to the PL in direct and indirect III–V materials. This phenomenon was reported from PL measurements of a 0.22% tensile strained, 1 \(\times 10^{19}\) cm\(^{-3}\) n-type doped Ge-on-Si. Ge is a well-known indirect band material, and L valley is the minimum of the conduction band. Due to the band-filling effect in the L valleys, the activation energy for direct band transition becomes smaller as doping concentration increases. As a result, more electron carriers are thermally excited from the L valleys to the Γ valley contributing to direct band transition in Ge as temperature increases [21]. The activation energy, \(E_a\), is defined as \(E_a = E_{\Gamma} - E_{\Gamma}^{\prime}\), where \(E_{\Gamma}\) is the direct conduction band edge, and \(E_{\Gamma}^{\prime}\) is the Fermi level. The activation energies of S02 and S03 are 79 and 65 meV, respectively, fitted from the Arrhenius plot of the integrated PL intensity versus temperature, as shown in Fig. 5. The direct conduction band edge of S01 is 31 ± 3 meV higher than that of S02, as previously mentioned, and its Fermi level is expected lower as it is for lightly n-type doping. Thus, the activation energy of S01 is expected to be larger than 110 meV, and carrier thermalization is more difficult to achieve than for in S02. Correlating with Fig. 4, besides high n-type doping concentration, small activation energies of S02 and S03 also enhance the carrier injections into their Γ valleys at room temperature. Additionally, it is also worth mentioning that some publications [24,25] referred the carrier thermalization as a negative thermal quenching effect, and a simplified fitting method was proposed to correlate the PL intensity with the temperature. However, the authors misinterpreted the origins of the observed PL emission peaks; therefore, their approach is not valid.

Figure 6 shows the room-temperature PL intensities and direct band energies of Te-doped Ga\(_{0.74}\)In\(_{0.26}\)P samples as a function of active doping concentration. It shows a linear relationship between the band energy reduction and the increase of doping concentration. This observation was also reported for highly n-type doped Ge at room temperature [26]. Although the linear fitting still uses a phenomenological model, it appears to be valid for both n-type doped indirect bandgap Ge and indirect III–V alloys. The direct band energy of the Ga\(_x\)In\(_{1-x}\)P sample with \(n = 2 \times 10^{18}\) cm\(^{-3}\) is 10 meV below the fitted curve. According to the numerical results of the major critical points for disordered Ga\(_x\)In\(_{1-x}\)P alloys in Ref. [27], the Ga content reduction of 2% in Ga\(_{0.74}\)In\(_{0.26}\)P caused an energy reduction of the Γ, X, and L bands by 11, 4, and 1 meV, respectively. In addition, XRD shows a small compressive strain (< 0.01%) in this sample, which is expected to increase its band energy by ~1 meV rather than reducing it. Thus, the composition shift caused Γ band energy reduction agrees well with the discrepancy in the linear fitting of Fig. 6.

![Fig. 4](image-url)  
**Fig. 4.** Temperature-dependent PL spectra (175–300 K) of Te-doped Ga\(_{0.74}\)In\(_{0.26}\)P samples with (a) S01, \(n = 7 \times 10^{16}\) cm\(^{-3}\), (b) S02, \(n = 9 \times 10^{17}\) cm\(^{-3}\), and (c) S03, \(n = 2 \times 10^{18}\) cm\(^{-3}\).

![Fig. 5](image-url)  
**Fig. 5.** Arrhenius plot of integrated PL intensity versus temperature for Te-doped Ga\(_{0.74}\)In\(_{0.26}\)P samples with \(n = 9 \times 10^{17}\) cm\(^{-3}\) (red dots) and \(n = 2 \times 10^{18}\) cm\(^{-3}\) (blue diamonds). The activation energies, \(E_a\), were derived from the fitted dashed lines.
approximately six times compared with the lightly doped sample. As tellurium is a large n-type dopant compared with other dopants (i.e., Si), it may distort the sublattices of III–V compounds and form non-radiative recombination centers at high Te-doping concentration. The cross-section TEM (XTEM) image in Fig. 7(a) shows that there are no extended defects found in the Ga_{0.74}In_{0.26}P film; only some dislocations are visible in the SiGe graded buffer. The high-resolution TEM image in Fig. 7(b) shows no indication of large dopant clusters or other defects. Additionally, TEM inspections under two-beam conditions at g = 022 and g = 004 confirmed these observations. Therefore, the Te-doping related defects are likely to be the point defects, which potentially can be detected by deep level transient spectroscopy, as was done for Te-doped GaP [29]. In future work, post-annealing and growth temperature optimization will be explored to suppress the formation of Te-related defects.

4. CONCLUSIONS

In conclusion, Te-doped indirect bandgap Ga_{x}In_{1−x}P films were deposited on GaAsP/GeSi/Si. The active doping concentration varied from $7 \times 10^{16}$ to $2 \times 10^{18}$ cm$^{-3}$. The temperature-dependent PL spectra show that the indirect-to-direct band transition occurs between 40 and 100 K, and the direct band emission dominates the room-temperature PL spectra. Due to the BGN effect, the separation energy between $\Gamma$ and X bands shrinks as Te-doping concentration increases. Because the activation energy for carrier thermalization is decreased as doping concentration increases, the carrier thermalization is significant in n-type doped indirect bandgap Ga_{x}In_{1−x}P samples with $n = 9 \times 10^{17}$ cm$^{-3}$ and $n = 2 \times 10^{18}$ cm$^{-3}$. Therefore, the doping promotes the carrier injection into the $\Gamma$ valley, which enhances the direct band transition. We show that the integrated PL intensity has been increased by five times for the Ga_{0.74}In_{0.26}P sample with $n = 9 \times 10^{17}$ cm$^{-3}$ compared with the lightly doped sample with $n = 7 \times 10^{16}$ cm$^{-3}$. The origin of the PL intensity degradation at high doping concentration is not fully understood, but the TEM results can exclude large dopant clusters. In addition, there is a linear relationship between the BGN and the increasing doping concentration, which agrees with the model used for highly n-type doped Ge.

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