ISSN 1330–0008
CODEN FIZAE4

TIME-RESOLVED PHOTOLUMINESCENCE SPECTRA OF $(Al_xGa_{1-x})_{0.51}In_{0.49}P$ ($x = 0.29$) ALLOY

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Received 5 December 2001; revised manuscript received 28 April 2003
Accepted 2 June 2003 Online 20 September 2003

Measurements of time-resolved photoluminescence (TRPL) spectra were made in a study of the optical properties of partially ordered quaternary $(Al_xGa_{1-x})_{0.51}In_{0.49}P$ ($x = 0.29$) alloy. Both excitation-wavelength dependence of lifetime and excitation-intensity dependence of lifetime show a wide distribution of carriers. In TRPL spectra measured at 300 K, a blue-shift of photoluminescence (PL) peaks in $(Al_xGa_{1-x})_{0.51}In_{0.49}P$ is observed. The phenomenon is in agreement with the Z-shaped temperature-dependence of the PL peak. Possible origins of the blue-shift and Z-shaped behaviour of PL peak are presented.

PACS numbers: 78.30.Fs, 78.55.-m, 71.23.-K UDC 535.37

Keywords: quaternary $(Al_xGa_{1-x})_{0.51}In_{0.49}P$ alloy, III-V semiconductors, ordered alloys, photoluminescence

1. *Introduction*

The quaternary compound $(Al_xGa_{1-x})_{0.51}In_{0.49}P$ alloy grown by metalorganic vapour phase epitaxy (MOVPE) is a promising candidate alloy for visible wavelength optoelectronic devices, such as solar cells, lasers and light-emitting diodes (LED) [1], since it has the largest direct band gap of GaAs lattice-matched semiconductor. For $x < 0.50$, $(Al_xGa_{1-x})_{0.51}In_{0.49}P$ shows a direct band gap character [2,3]. Many investigations have been carried out on the properties of the end ternary with $x = 0$ GaInP alloys, which can spontaneously form a CuPt-type ordered structure which is considered to be made up of a composite of ordered domains in a disordered matrix in the [111] direction. Compared with disordered GaInP, which has a higher luminescent efficiency, the ordered GaInP displays some special properties: the band-gap shrinkage, the occurrence of multi-peaks and the blue-shift effect of photoluminescence (PL) peak with the increase of the excitation intensity. These unique properties and features closely vary with growth conditions [4–10] including methods of growth, substrate temperature, growth rate, substrate orientation, nutrient phase stoichiometry, carrier gas and so on. The ordered alloy shows different features even though the alloy composition is fixed. The long-range ordered structure has also been found in AlGaInP alloys. Kowalski et al. [1] have reported the order-induced splitting of normally degenerate zone-center valence-band states relevant to the order-induced band-gap reduction by polarized spectroscopy. Asahi et al. [11] and Suzuki et al. [12] also demonstrate the existence of band-gap anomaly and sublattice ordering by measuring the valley-to-peak height ratios in Raman modes. We have also reported an anomalous blue-shift of PL peak of temperature-dependent spectra of $(\mathrm{Al}_x\mathrm{Ga}_{1-x})_{0.51}\mathrm{In}_{0.49}\mathrm{P}$, which occurs in the 55−84 K region. The profile of the PL peak of the whole temperature region displays as a Z-shape. We deduced the result on the band-folding effect of conduction band from the L band to the Γ band due to the influence of superlattice effect of ordered structure [13]. However, there are few reports on the time-resolved photoluminescence (TRPL) process of $(\mathrm{Al}_x\mathrm{Ga}_{1-x})_{0.51}\mathrm{In}_{0.49}\mathrm{P}$ to date. In this study, we applied the TRPL investigation on the partially ordered $(\mathrm{Al}_x\mathrm{Ga}_{1-x})_{0.51}\mathrm{In}_{0.49}\mathrm{P}$ alloy and directly observed the process of the transfer of carriers and the blue-shift of PL peak in $(\mathrm{Al}_x\mathrm{Ga}_{1-x})_{0.51}\mathrm{In}_{0.49}\mathrm{P}$.

2. Experiment

The sample used in this study was grown by metalorganic vapour phase epitaxy on Si-doped GaAs substrate on 6^0B plane. The growth temperature was 700 °C, the V/III ratio was kept at a value of 100. The $(\mathrm{Al}_x\mathrm{Ga}_{1-x})_{0.51}\mathrm{In}_{0.49}\mathrm{P}$ layer thickness was 1 μm after the 15 minutes growth. The growth conditions have been proven to yield ordered materials relatively easily [7,8]. The lifetime decay and TRPL spectra were measured at room temperature and in a liquid-nitrogen cryostat. For the decay measurements, the detection wavelength was set at the PL peaks.

The output of a cavity-dumped dye laser (570–640 nm), synchronously pumped by a doubled-frequency cw mode-locked Nd^{3+}:YAG laser (Spectra-Physics Inc., series 3000), was used in the experiment to excite the sample. Neutral filters were used to change the excitation intensity. The PL signals were detected through a lens system at the slit of a spectrograph, from which the dispersed spectrum was thereafter time-resolved by a synchronous streak camera (Hamamatsu Inc., Model C1587), and finally detected by a CCD. The time resolution of the whole system was limited by dye lasers to about 10 ps.

3. Results and analyses

The sample has the direct band-gap character and shows CuPt-type partially-ordered structure as described in our previous work [13]. Figure 1 shows two typical

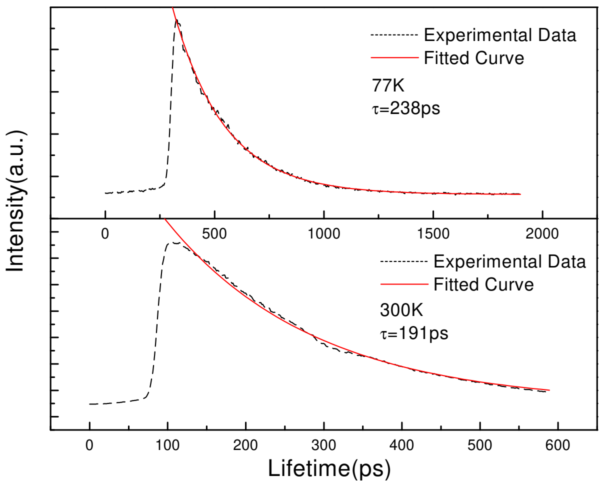

Fig. 1. Luminescence decay of AlGaInP *alloy at 77* K *and 300* K*, respectively, fitted by* $y = y(0) + Ae^{-t/\tau}$.

luminescence decays of $(Al_xGa_{1-x})_{0.51}In_{0.49}P$ alloy at 77 K and 300 K, respectively. The dots show the experimental data and the solid line is the fitted curve. Using the classical law of decay of single-exponential time dependence

$$I = Ae^{-t/\tau}$$

to fit the experimental data, where τ is the time constant and A stands for the luminescent intensity at $t = 0$, we found the lifetimes of $(Al_xGa_{1-x})_{0.51}In_{0.49}P$ to be 238 and 191 ps at 77 K and 300 K, respectively. Laser pulses with different wavelengths were used to excite the sample. The lifetime is sublinearly dependent on the excitation wavelength as shown in Fig. 2.

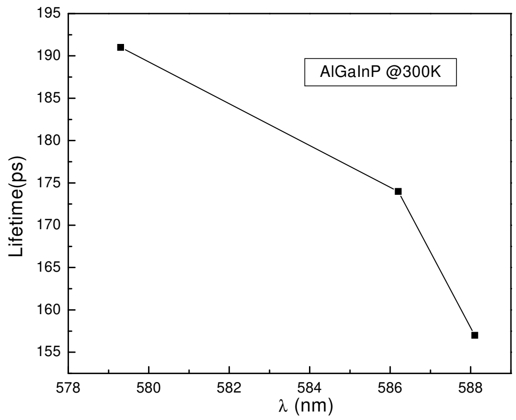

Fig. 2. Excitation – wavelength dependence of lifetime of AlGaInP *alloy at 300* K.

Figure 3 shows the dependence of lifetime on excitation intensity measured at 77 K and 300 K, which also shows sublinear dependence. Figures 2 and 3 demonstrate that the carriers distribute over rather wide bands.

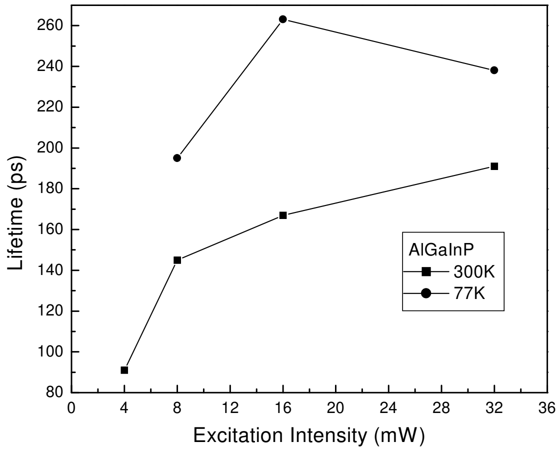

Fig. 3. Excitation – intensity dependence of lifetime of AlGaInP *alloy at 77* K *and 300* K*, respectively.*

Figure 4 shows the TRPL spectra of AlGaInP alloy at 77 K and 300 K. With the time delay, the PL peaks almost remain unchanged at 77 K, while at 300 K, there is a small blue-shift of approximately 8 meV, which is contrary to the character of donor-acceptor pairs (DAP). From Fig. 4, one can also see that the PL peak energy has a rather big increase at 300 K compared to that at 77 K. One possibility of such blue-shift in TRPL spectra is that AlGaInP has longer lifetime at shorter wavelength. With the delay of time, the blue-side of the PL decreases slower than the red-side so that the blue-shift occurs. Even so, it is difficult to explain why the blue-shift does not happen at 77 K. In addition, it is difficult to give a reasonable explanation for the increase of the PL-peak energy at 300 K compared to that at 77 K. In our previous work, we reported a Z-shaped temperature dependence of the PL peak [13]. The PL peak energy decreases when increasing temperature from 19 K, a blue-shift of PL peak energy occurs between 55 K and 84 K, while at higher temperatures, the PL peak energy decreases monotonously again. We suppose that such Z-shaped temperature-dependence is due to the band-folding effect of superlattice of ordered structure. The blue-shift phenomenon in TRPL spectra is coincident with the Z-shaped PL temperature dependence. Taken these two phenomena into consideration together, it seems more likely that the blue-shift effect in TRPL spectra derives from the band-folding effect of superlattice of ordered structure. Ordered structure, which is also the so-called orientational superlattice structure [14], is considered as a composite of the low-band-gap ordered domains in a high-band-gap disordered matrix [5] and leads to the occurrence of sub-bands. In other words, the L-band is folded to the Γ-band in the Brillouin zone due to the superlattice effect. The transfer of carriers from the Γ-band to the L-band during the decay time leads to the blue-shift in TRPL spectra.

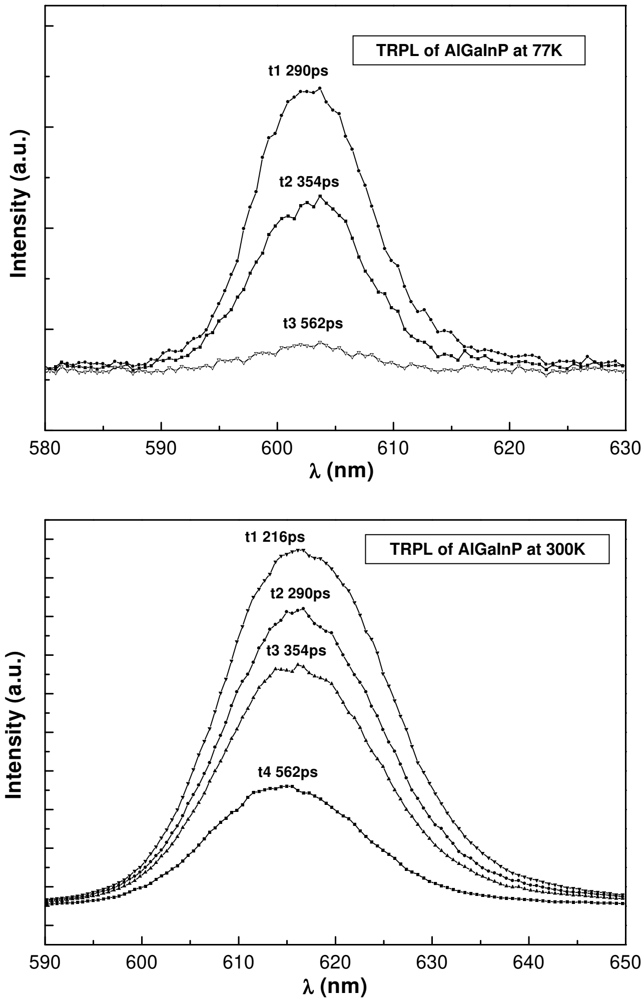

Fig. 4. Time-resolved photoluminescence spectra of AlGaInP *alloy at 77* K *and 300* K.

The single-exponential component fitting equation also suggests the same category of carriers of the Γ- and L-band. The transfer of carriers is more apparent at 300 K. This is because the blue-shift of PL peak occurs in the 55−84 K region, given the band-folding effect, the L-band lies above the Γ-band, the carriers of the Γ-band are still rather stronger than those of the L-band at 77 K. While at 300 K, due to the thermal quenching and the blue-shift effect, the luminescence is dominated by the L-band, it is relatively easier for the carriers to get energy to transfer from Γ band to L band at higher temperature, so the transfer becomes more apparent correspondingly. The small blue-shift also indicates a small separation of L- and Γ-band so that the transfer of carriers is possible. Hence, this phenomenon seems to verify our conjecture of band-folding effect of the conduction band from the L-band to the Γ-band.

However, the anomalous Z-shaped PL behaviour is also observed in quantum-dot samples and InGaN materials, where there no band-folding occurs. That behaviour appears to be a result of the microscopic nature of the alloy, either due to a compositional fluctuation or the domain nature of ordered and disordered domains. Since the Z-shaped phenomenon also occurs in other AlGaInP samples with different degree of order, the compositional fluctuation can probably be ruled out. The microstructure of ordered samples has been shown to consist of domains characterized by different order parameters and/or alternate order plane orientations. Additionally, there exist "anti-phase boundaries" between domains with a phase shifted order plane alignment [15]. Such domains or domain boundaries are expected to play an important role in the recombination dynamics as well as in the origin of Z-shaped PL behaviour. Which of the aboved mentioned explanations is the proper one can not be answered on the basis of the presented investigation. Further study is needed to distinguish the ambiguities.

4. *Conclusion*

The TRPL spectra were studied in an investigation of the optical properties of partially ordered quaternary $(Al_xGa_{1-x})_{0.51}In_{0.49}P$ ($x = 0.29$) alloy. Both excitation-wavelength dependence of lifetime and excitation-intensity dependence of lifetime show a wide distribution of carriers along bands. In TRPL spectra measured at 77 K and 300 K, with the delay of time, the PL peaks remain almost unchanged at 77 K, while at 300 K, there is a small blue-shift, which is coincident with the Z-shaped PL temperature-dependent measurement. The origin of the blue-shift and Z-shaped PL phenomenon is attributed to either the band-folding effect of conduction band from the L-band to the Γ-band of the ordered structure or to the domain nature associated with the ordered structure. Further study is needed to distinguish the ambiguities.

Acknowledgements

The authors would like to thank the cooperation of the State Key Laboratory of Optoelectronic Materials and Technologies of Zhongshang University. This work is supported by the National Natural Science Foundation of China (Grant No. 60276002), and partly supported by the Natural Science Foundation of Fujian Province of China (Grant No. A0110007).

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VREMENSKI RAZLUČENI FOTOLUMINESCENTNI SPEKTRI LEGURE $(Al_xGa_{1-x})_{0.51}In_{0.49}P$ ($x = 0.29$)

Načinili smo vremenski-razlučena (VR) mjerenja fotoluminescentnih (FL) spektara radi istraživanja optičkih svojstava djelomično sređene četverokomponentne legure $(Al_xGa_{1-x})_{0.51}In_{0.49}P$ ($x = 0.29$). Obje ovisnosti vremena života, uzbuda – valna duljina i uzbuda – intenzitet pokazuju široku raspodjelu nositelja. VR FL spektri $(Al_xGa_{1-x})_{0.51}In_{0.49}P$ na 300 K pokazuju plavi pomak fotoluminescentnih linija. Ta je pojava u skladu s temperaturnom ovisnošću FL vrha u vidu slova Z. Raspravljaju se mogući uzroci plavog pomaka i Z-ovisnosti FL vrha.