Time-resolved photoluminescence study of $Ga_{0.52}In_{0.48}P$ alloys

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Abstract. The time-resolved photoluminescence spectra of ordered and disordered $Ga_{0.52}In_{0.48}P$ alloys were studied at room temperature and at 77 K liquid nitrogen, respectively. The ordered samples have well fitted two exponential processes decay curves and the time constants are sample dependent and have little relationship with the ordering degree. The decay curve of disordered sample shows that it has single exponential process and its lifetime has a tendency of reduction with the decrease of excitation intensity. The photoluminescence spectra with different delay time at 77 K show that the ordered samples exhibit about $6 \sim 10$ meV blue-shift of PL peak energy with the delay time.

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1 Introduction

The ternary III-V alloys of $Ga_xIn_{1-x}P$ have attracted a great deal of attentions for the past decade as a promising material of optoelectronic devices such as solar cells [1] and laser diodes [2]. The properties of $Ga_xIn_{1-x}P$ alloys have been shown to critically depend on growth parameters [3], such as growth rate, V/III ratio, substrate temperature and orientation. Under different growing conditions, $Ga_xIn_{1-x}P$ can form ordered or disordered structure. Generally, $Ga_xIn_{1-x}P$ grown by liquid phase epitaxy(LPE) shows disordered character with band gap of $1.9 \sim 1.92$ eV at room temperature, in which the group-III atoms of Ga and In randomly distribute on the group-III sublattice. While grown by metal organic vapor phase epitaxy (MOVPE) [4] or molecular beam epitaxy (MBE) [5], $Ga_xIn_{1-x}P$ can form a long-range CuPt-type ordered structure [6,7] spontaneously, with alternating Ga- and In-rich planes along the $(\bar{1}11)$ and the $(1\bar{1}1)$ direction. The optical properties of ordered $Ga_xIn_{1-x}P$ alloys are different from that of disordered $Ga_xIn_{1-x}P$ alloys. For ordered $Ga_xIn_{1-x}P$, the band gap is about $1.8 \sim 1.9$ eV at room temperature with a reduction of $50 \sim 100$ meV compared with disordered alloys. The band-gap reduction is usually explained in terms of the folding of electronic states, at L point in the random alloy, to the zone center, which then repel the valence band upwards and the conduction band downwards [8]. In addition to the band gap reduction, there are other unique optical properties such as multiple PL peaks, the strong excitation intensity [9] and temperature [10] dependence of the PL spec-

tra at low temperature. For the case of double peaks, the high energy peak is regarded as due to the recombination of band edge exciton [11] which is independent of the excitation intensity while the low energy peak, which is defect related but its origin is not well understood, has strong dependence of the excitation intensity [12]. Although the band gap reduction has limited the application of ordered $Ga_xIn_{1-x}P$ related optoelectronic devices to shorter wavelength ranges, it is still an attractive alternative to AlGaAs in optoelectronic devices for these reasons: lattice matched to GaAs, large valence-band discontinuity, wide direct E_g, low surface recombination with GaAs and smooth inverted heterointerfaces. Moreover, the two band-gap states of $Ga_xIn_{1-x}P$ can be used in band-gap engineering: disorder-order-disorder (d-o-d) light-emitting diods [13] and d-o-d quantum wells [14]. Also the o-d modulation-doped junctions [15] have been reported.

In this paper, we report on the measurement of the time-resolved spectra of ordered and disordered $Ga_xIn_{1-x}P$ $(x = 0.52)$ at room temperature of 300 K and at liquid nitrogen temperature of 77 K, respectively.

2 Experiments

The samples were grown by MOVPE on GaAs substrate 6^0 misoriented toward $[111]_B$ direction for ordered samples and toward $[111]_A$ for disordered sample. The time-resolved photoluminescence (TRPL) measurements were carried out using a picosecond pulse laser system (Spectra-Physics Inc., series 3000), with the 532 nm line of a doubled-frequency cw mode-locked Nd:YAG laser for sample excitation and the laser excitation intensity was
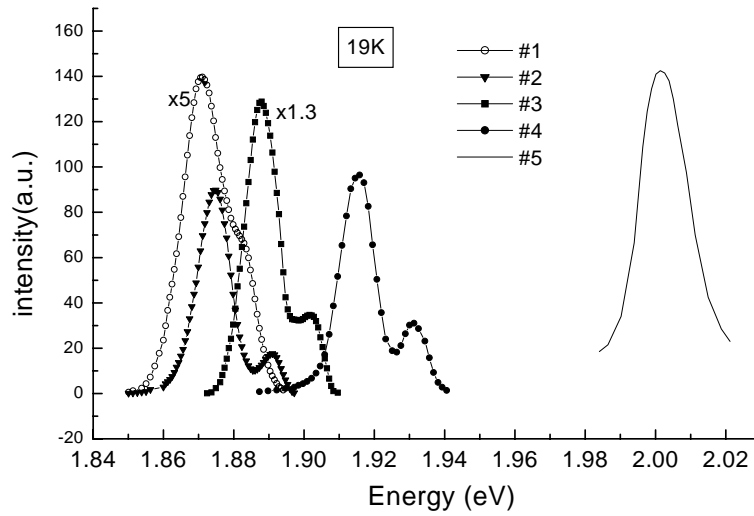
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Fig. 1. Photoluminescence spectra of ordered and disordered GaInP at 19 K.

30 mW both at 77 K and room temperature. The pulse repetition of the laser was 82 MHz and the pulse width was 60 ps. Neutral filters were used to change the excitation intensity when measured the excitation intensity dependence of the decay lifetime. The samples were put into 77 K nitrogen liquid cryostat for low temperature measurement. The PL signals were collected 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 ordered samples are named as #1, #2, #3, #4, and disordered #5. For ordered samples, the ordering degree is, #1 and #2 the greatest, #3 the moderate and #4 the smallest.

3 Results and discussions

Figure 1 shows the photoluminescence spectra of the samples at 19 K [16] in our previous work. The ordered samples exhibit two peaks at temperature lower than 80 K: the high energy peak is independent of the excitation intensity while the low energy peak has a blue-shift with the excitation intensity increases. When the temperature is up to about 80 K, the low energy peak thermally quenches. In fact, all the ordered samples in this work were measured both at 77 K and at room temperature, only the high energy peak which is usually regarded as the band edge excitonic transition can be detected. Then, in our experiment, all the luminescence decays of ordered samples were measured at this peak energy. The typical luminescence decay profiles of ordered and disordered $Ga_{0.52}In_{0.48}P$ are shown in Figures 2 and 3 at 77 K and with the laser excitation intensity of 30 mW. The decay curves of ordered samples can be well fitted with two exponentials. The fitted equation is

$$A = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$$

where τ_1 and τ_2 are the time constants of the rapid and slow processes and A_1, A_2 are the intensity of the
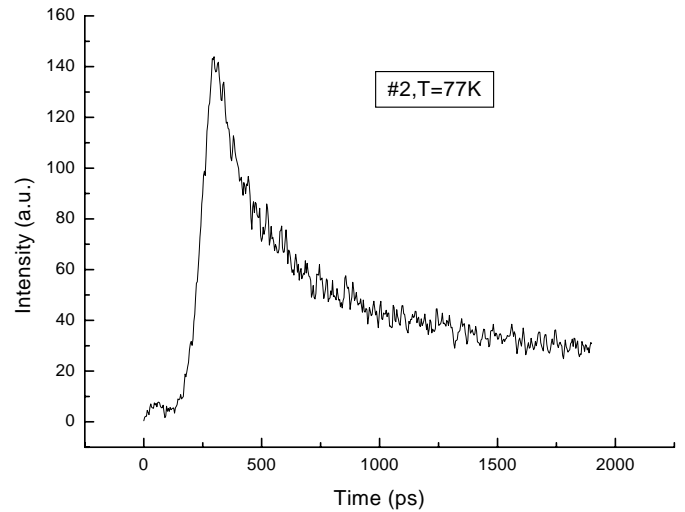

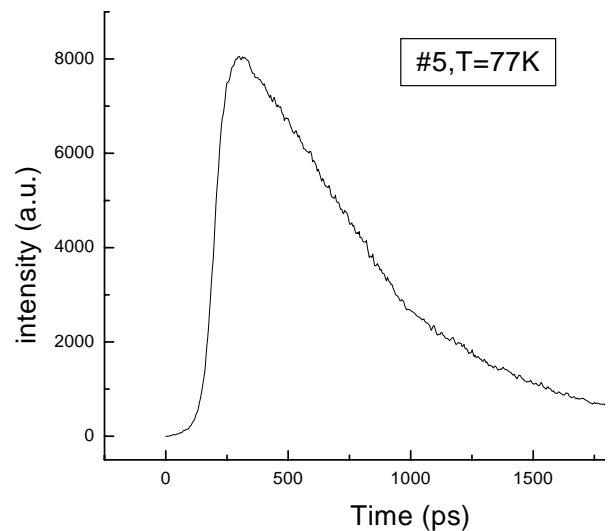**Fig. 2.** Luminescence decay of ordered GaInP at 77 K.

Fig. 3. Luminescence decay of disordered GaInP at 77 K.

corresponding processes, respectively. The fitted time constants are shown in Table 1 from which we can see the ordered samples have a wide range of time constants that have little relationship with the ordering degree. At 77 K, τ_1 is about $168 \sim 579$ ps and τ_2 is above nanoseconds. With the increase of temperature, the intensity of nonradiative recombination becomes stronger and then both of the two processes become faster. At room temperature, τ_1 is about $155 \sim 246$ ps and τ_2 about $327 \sim 1832$ ps. The intensity of fast emission A_1 is one order of magnitude than that of slow emission A_2 both at room temperature and at 77 K, indicating that the recombination of the short lifetime emission dominates the luminescence decay.

For the disordered sample, the measured energy was set at the PL peak energy of 1.937 eV at room temperature and 2.015 eV at 77 K. The decay curve can be fitted with single exponential and the time constant is 219.5 ps at room temperature and 287.1 ps at 77 K, respectively.

The luminescence decays were measured with the reduction of the laser excitation intensity. The results of ordered samples show that the short lifetime τ_1 is independent of the excitation intensity both at room temperature and at 77 K. Also the long lifetime τ_2 is independent of the excitation intensity at 77 K. While at room temperature it is weakly dependent on the excitation intensity and has a tendency of reduction with the increase of the excitation intensity.

As for excitation intensity dependence of the disordered sample, the lifetime becomes shorter reducing the excitation intensity, which is different from τ_1 and also shows opposite behavior to τ_2 of the ordered samples at room temperature.

The photoluminescence spectra of ordered samples with different delay time were carried out. The PL peak at 77 K moves to the higher energy about 6–10 meV with the delay of time, as shown in Figure 4 (the laser excitation intensity is 30 mW). The delay time, t_1, t_2, t_3, t_4, t_5 are 119 ps, 216 ps, 290 ps, 353 ps and 561 ps, respectively. This phenomenon has never been observed before. The value of blue-shift of PL peak with the delay time is sample dependent and likely related with ordering degree. The PL peak energy of samples #1 and #2 with the greatest ordering degree has a blue-shift about 10 meV with the delay time from t_1 to t_5 and the sample #4 with the smallest ordering degree has a blue-shift of about 6 meV with the same delay time. However, this blue-shift of ordered samples at room temperature is hardly detected. The photoluminescence spectra of disordered sample with different delay time were detected as well but the peak energy shows no blue-shift with the delay time both at room temperature and at 77 K. The blue shift of ordered samples might suggest two situations: one is that the decay of carriers in lower energy side is faster than those in higher energy side (normally one observes the opposite case: the carriers in the higher energy side decay faster), and the other is that the carriers in lower energy side are thermally excited to higher energy. But the real origin of this blue-shift should be subjected to further discussions.

Table 1. The fitted time constants of ordered samples.

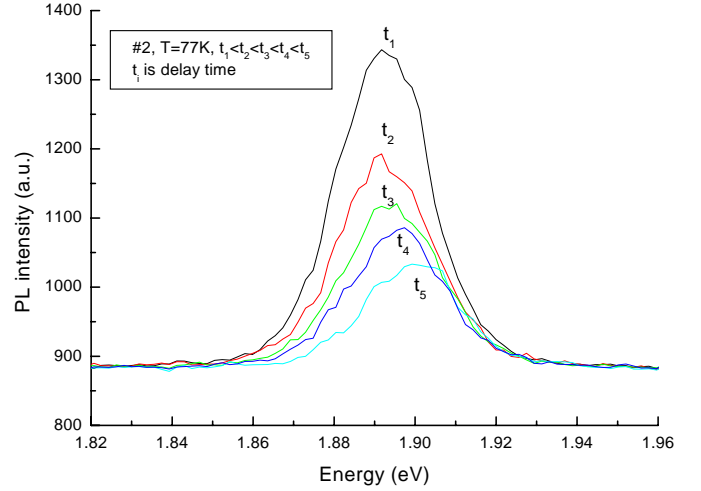|	τ_1 (ps)		τ_2 (ps)	
sample	77 K	300 K	77 K	300 K
#1	578.6	186.7	4588.1	1072.3
#2	167.9	155.3	1838.9	327.4
#3	546.8	230.2	4994.5	1377.1
#4	295.9	246.5	4438.2	1832.3

Fig. 4. Tthe PL spectra of #2 with different delay time at 77 K.

4 Conclusion

Time-resolved photoluminescence spectra of ordered and disordered $Ga_{0.52}In_{0.48}P$ were measured at 77 K and at room temperature. The decay curves of ordered samples can be well fitted with two exponential processes. At 77 K, the time constants of τ_1 and τ_2 are $168 \sim 579$ ps and above nanoseconds. At room temperature, they are $155 \sim 246$ ps and $327 \sim 1832$ ps, respectively. The lifetime is almost independent of the laser excitation intensity especially at 77 K. Another interesting phenomenon is that the photoluminescence peak energy exhibits a blue-shift of 6–10 meV with the delay time at 77 K.

The time-resolved photoluminescence properties of disordered sample are quite different from those of the ordered samples. On one hand, the decay curve can be fitted with single exponential and the lifetime has a tendency to reduction with the decrease of the laser excitation intensity. On the other hand, the photoluminescence peak energy has no blue-shift with the delay time both at 77 K and at room temperature.

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